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SUMMARY

Potassium superoxide, KO_2, has been used extensively to supply oxygen (O_2) and scrub carbon dioxide (CO_2) in a variety of ambient-pressure life-support applications. Potassium superoxide is currently being considered for use as the air-revitalization chemical in portable, hyperbaric, life-support systems. However, in portable breathing apparatus applications at 1 atm, KO_2 has exhibited low utilization efficiency of the available O_2 and diminished CO_2-scrubbing capacity because of the formation of a fused, hydrated-hydroxide/carbonate coating on the superoxide granules. This poor utilization of the KO_2 has resulted in larger, heavier breathing apparatus than would be required if a superior dual-purpose chemical could be developed.

In earlier work it was discovered that granules fabricated from an intimate mixture of KO_2 and calcium superoxide, $Ca(O_2)_2$, did not exhibit formation of a fused product coating, and the utilization efficiency with respect to both O_2 release and CO_2 absorption was superior to KO_2 granules when both types of granules were reacted with humidified CO_2 under identical conditions. However, no evaluation of the reactivity of these superoxide mixtures at hyperbaric pressures had been carried out.

In the work described here, single pellets of KO_2 and $KO_2/Ca(O_2)_2$ mixtures and commercially available KO_2 tablets and granules were reacted with a flow of humidified CO_2 in helium at total pressures of 1 and 10 atm and at an initial temperature of 40°C. In the 1-atm flow tests, the reaction rates and utilization efficiency of the $KO_2/Ca(O_2)_2$ pellets was markedly superior to the KO_2 pellets, tablets, and granules when the samples were reacted under identical conditions. However, at 10 atm, the rates of O_2 release and CO_2 absorption as well as the utilization efficiencies of all the superoxide sample types were one-third to one-eighth of the values observed at 1 atm. The decrease in reaction performance at 10 atm compared to that seen at 1 atm has been attributed principally to the lower bulk diffusivity of the CO_2 and H_2O reactants in helium at the higher pressure and secondarily to the moderation of the reaction temperature caused by the higher heat capacity of the 10-atm helium.

INTRODUCTION

Historical and Technical Background

Superoxides in portable life-support systems- Superoxides have been used extensively to supply oxygen (O_2) and scrub carbon dioxide (CO_2) in a variety of ambient-pressure life-support applications, including portable, self-contained breathing apparatus (ref. 1); spacecraft (ref. 2); and undersea submersible craft (refs. 3 and 4). Superoxides are potentially attractive candidates for use in hyperbaric air-revitalization applications because of their high O_2 storage density, and the potential simplicity of the total O_2 delivery/CO_2-scrubbing system (ref. 5).

The current state of the art in closed-cycle, backpack life-support systems for free-swimming divers reaching depths of ~120 m relies on a helium-oxygen gas-mixture blending system which maintains the partial pressure of oxygen, pO_2, at a constant level by sensing the pO_2 and adjusting the level upward by opening a valve to a high-pressure O_2 bottle (ref. 6). This continual ability to adjust the pO_2 enables the diver to remain in an O_2 concentration regime which avoids both hypoxia and O_2 toxicity during the dive to lower depths, and upon the return to the surface during decompression. Carbon dioxide is absorbed in this system by using a cartridge containing barium and calcium and potassium hydroxides (i.e., baralime). Similar systems are used in hyperbaric diving chambers (ref. 7).

There are several potential advantages for using a chemically stored O_2 source such as a superoxide which also scrubs CO_2 in a hyperbaric life-support system. First, superoxide-based air-revitalization systems are automatically demand-responsive since the amounts of the key reactants (water vapor (H_2O) and CO_2 in the user's exhaled breath) reaching the chemical bed increase as the user's ventilation volume increases. Therefore, simplification of the overall system and reliability enhancement would be possible through the elimination of valves and sensors. Secondly, since the CO_2-absorber bed would be replaced by the superoxide bed and no large O_2 storage tank would be required, the overall volume of the backpack or subsystem could be reduced. Alternatively, the duration of use of the backpack breathing system could be increased without significantly increasing the size. Finally, since the reaction of superoxides with humidified CO_2 is exothermic (releases heat), heating of the inhaled gas to prevent hypothermia in frigid waters could be reduced or eliminated if the rates of the superoxide-H_2O and superoxide-CO_2 reactions at hyperbaric pressures are similar to those observed at 1 atm.

Potassium superoxide in life-support systems- The superoxide which has been most widely used for air-revitalization purposes has been potassium superoxide, KO_2. The popularity of KO_2 is probably due to its high reactivity with respiratory gases, its thermal stability and long shelf-life, and the fact that it is commercially available in high purity. The reactivity of KO_2 with expired respiratory gases at atmospheric pressure is fairly well understood. Potassium superoxide has been used extensively as the life-support chemical in coal mine rescue-team breathing devices, and also has been incorporated into self-contained, self-rescuers for coal miners (refs. 1 and 8). Utilizing KO_2 as the air-revitalization chemical in portable life-support systems is the most challenging life-support application of this superoxide because of the stringent weight and volume requirements of the portable system, and the fact that the KO_2 bed is exposed to a high partial pressure of H_2O (i.e., up to 47 mm Hg).

Problems with potassium superoxide- The use of KO_2 as an air-revitalization chemical in portable life-support systems has been hampered by several problems. First, upon exposure to the concentrations of H_2O and CO_2 existing in exhaled human breath, KO_2 tends to form a fused, hydrated-hydroxide/carbonate coating on the exterior of the chemical which can greatly limit further utilization of the chemical. In addition to the coating barrier on the granules, intergranule fusion can take place which blocks off entire sections of the superoxide bed from further contact with the exhaled gases, thereby greatly increasing the pressure drop through the bed. This formation of fused, hydrous coatings results in chemical utilization efficiencies of only 50-80% (ref. 9), thus requiring larger KO_2 beds than would be necessary if higher utilization efficiencies could be achieved.

Secondly, KO_2 over produces O_2 relative to the amount of CO_2 it absorbs in portable life-support systems. The reason for this is as follows. If it is assumed that potassium carbonate, K_2CO_3, is the sole CO_2/KO_2 reaction product, then the theoretical ratio of CO_2 absorbed to O_2 evolved for pure KO_2 is 0.67. This assumption is reasonable since under the high-temperature (>130°C) reaction conditions existing in the KO_2 bed of a portable life-support system, potassium bicarbonate ($KHCO_3$) is not thermally stable; therefore, it is not a significant O_2 reaction product. Since the respiratory quotient, RQ (i.e., the volume of CO_2 eliminated divided by the volume of O_2 taken up) of humans engaging in moderate work ranges from 0.8 to 1.0 (ref. 10), it is apparent that to meet the metabolic requirements of humans, the KO_2 bed has to be oversized to match the CO_2-absorbing requirement, or additional CO_2-absorber capacity must be provided. While it is true that in diving applications the absorption of CO_2 as $KHCO_3$ could possibly be enhanced by moderating the temperature of the KO_2 bed using a heat exchanger, such cooling would probably have a detrimental effect on the rates of O_2 evolution and CO_2 absorption and on the utilization efficiency of the KO_2 (refs. 6 and 11).

Overcoming the problems with potassium superoxide- In the past there have been two main approaches to solving the problems associated with the use of KO_2 as a life-support chemical. In the first approach, engineering solutions to the fusing of the chemical have been sought through changing the KO_2 bed configuration. This was done either by changing the bed dimensions, or by sectioning the bed into multiple thin layers of KO_2 (ref. 3). The second approach has been to dilute the KO_2 bed with granules of other materials such as molecular sieve desiccants or CO_2 absorbents (refs. 8 and 12). Neither of these approaches has been completely successful, especially in portable breathing-apparatus applications. Therefore, state-of-the-art portable breathing devices employing KO_2 carry up to twice as much KO_2 than is theoretically required to meet the metabolic requirements of the user (ref. 13). The size of the KO_2 bed has a direct impact on the overall weight and bulkiness of the portable breathing device.

In response to these problems with KO_2, a search has been made for alternate dual-function chemicals which could be used in place of KO_2 as air-revitalization agents. Three main classes of chemicals have been evaluated as potential candidates for replacement of KO_2; alkali and alkaline earth metal peroxides, superoxides, and ozonides (ref. 14). Most of the compounds in these three classes of chemicals can be eliminated for one or more of the following reasons:

1. The compounds are unstable at ambient temperatures (e.g., all ozonides and lithium superoxide) (refs. 15 and 16).

2. The compounds possess no advantage over KO_2 in terms of O_2 capacity and CO_2-scrubbing capacity per unit weight (e.g., all peroxides except lithium peroxide, and strontium, barium, rubidium, and cesium superoxides).

3. The compounds exhibit problems of fused coatings similar to those shown by KO_2 (e.g., alkali metal superoxides).

4. The compounds exhibit an unfavorable ratio of CO_2 absorbed to O_2 released, such that either additional O_2-releasing chemicals would have to be provided (e.g., lithium peroxide) or additional CO_2-scrubbing capacity would need to be provided (e.g., all ozonides) for optimum performance.

Work on calcium superoxide- One compound that is not excluded by these criteria is calcium superoxide, $Ca(O_2)_2$, and for that reason, it has received considerable study, both in the United States and in the Soviet Union (refs. 15 and 17). In research done at NASA Ames Research Center on the synthesis of $Ca(O_2)_2$ (refs. 18-21), the highest purity (67%) preparation of the chemical reported in the literature was obtained, and two patents on the synthesis process have been granted (refs. 22 and 23). Since the major impurities in $Ca(O_2)_2$, calcium peroxide (CaO_2), and calcium hydroxide ($Ca(OH)_2$) release O_2 and/or absorb CO_2, the theoretical ratio of CO_2 absorbed to O_2 released by the chemical containing 67% $Ca(O_2)_2$ corresponds closely to the RQ of a human engaging in moderate work (i.e., 0.8-1.0). The amount of available O_2 in this moderate purity $Ca(O_2)_2$ is equivalent to that in commercial, 90% KO_2. Also, since the reaction product of $Ca(O_2)_2$ with H_2O, $Ca(OH)_2$, is nonhygroscopic and decomposes at a high temperature without melting, use of $Ca(O_2)_2$ in air-revitalization applications is not hampered by the formation of fused, hydrous coatings. These factors make $Ca(O_2)_2$ an attractive replacement for KO_2. However, recent work on the reactivity of $Ca(O_2)_2$ with humidified CO_2 indicates that the major obstacle to the use of $Ca(O_2)_2$ in air-revitalization systems is finding a catalyst that will improve the rate of CO_2 absorption and will allow CO_2 absorption to occur simultaneously with O_2 release (refs. 13 and 24).

Superoxide mixtures- It was mentioned previously that improvement in the reaction behavior of KO_2 has also been sought by mixing granules of KO_2 with granules of other materials (ref. 12). These mixed granule beds were not significantly different in reaction properties from pure KO_2 beds and in many cases exhibited poorer performance. Very little work has been done on improving the reactivity of KO_2 by mixing it with other chemicals prior to the fabrication of granules or pellets, and most of this work has focused on adding transition metal catalysts (such as copper oxychloride and potassium permanganate to KO_2 to improve the rate of the oxygen release reaction (25). Some work has been done on adding alkali metal hydroxide and peroxides to KO_2 before the chemical was fabricated into rippled plates for use in a large chamber life-support system (ref. 25). The addition of lithium hydroxide to KO_2 improved the O_2 utilization efficiency, but the total O_2 yield was lower and no improvement in CO_2-absorption capacity over pure KO_2 was observed. It is not clear from the work described in reference 25 how well the KO_2-additive mixtures were blended prior to fabrication into the rippled plates.

During the course of research aimed at finding a catalyst for $Ca(O_2)_2$, it was discovered that granules fabricated from an intimate mixture of KO_2 and $Ca(O_2)_2$ powder may be a very promising replacement to pure KO_2. Preliminary work conducted at Ames on the reactivity of granules fabricated from an intimate mixture consisting of 75% KO_2 and 25% $Ca(O_2)_2$ indicated that there was no evidence of fused hydrous coatings, and the utilization efficiency of the chemical with respect to both O_2 release and CO_2 absorption was up to 35% greater when compared to KO_2 granules prepared and reacted under identical conditions (ref. 13). It was postulated that the $Ca(O_2)_2$ aids the reactivity of KO_2 by bonding with excess moisture and preventing the formation of fused hydrated-hydroxide/carbonate coatings. The KO_2 is believed to enhance the reactivity of $Ca(O_2)_2$ by acting as a catalyst for the reaction of CO_2 with $Ca(OH)_2$ and CaO_2 (ref. 5). Since $Ca(O_2)_2$ also releases O_2 and scrubs CO_2, the overall O_2 capacity of the superoxide mixture is nearly identical to KO_2. By adding $Ca(O_2)_2$ to KO_2 in the proper proportions it might be possible to increase the ratio of CO_2 absorbed to O_2 released such that it more closely matches the RQ of man engaged in moderate activity.

However, these $KO_2/Ca(O_2)_2$ mixtures have not been tested at hyperbaric pressures. In fact, there has been no work reported in the literature in which canister-sized granules of any superoxide have been tested at pressures up to 10 atm. Therefore, it was felt that further research on these mixed superoxide materials would be necessary to determine if they would be suitable dual-purpose hyperbaric air-revitalization chemicals. In addition, it was felt that the proper evaluation of these $KO_2/Ca(O_2)_2$ mixtures would require that similar hyperbaric reaction data be obtained for commercial purity KO_2.

Objectives of the Research Program

The main goal of this program was to determine the composition of the mixture of KO_2 and $Ca(O_2)_2$ which would give the greatest improvement in reaction performance relative to commercial purity KO_2 when the materials were reacted with humidified CO_2 at hyperbaric pressures. An improvement in reaction performance was determined from a comparison of: (1) the rates of O_2 release and CO_2 absorption, (2) the utilization efficiency (i.e., the extent of utilization of the O_2 evolution and CO_2-scrubbing capacities), and (3) the physical characteristics (i.e., evidence of fused hydroxide/carbonate coating) exhibited by the $KO_2/Ca(O_2)_2$ and KO_2 samples during reaction with humidified CO_2. Evaluation of the mixed superoxides was accomplished on the flow system described below by reacting the superoxide granules with humidified carbon dioxide/helium gas mixtures under conditions simulating those existing in a manned, portable closed-circuit breathing apparatus (ref. 21). The evaluation of the mixtures was carried out at pressures of 1 and 10 atm. Tests at 1 atm gave baseline data to which the hyperbaric test data could be compared. A number of tests of KO_2 pellets and commercial KO_2 tablets and granules were conducted to provide data with which to compare and evaluate the reaction performance of the $KO_2/Ca(O_2)_2$ mixture pellets. The tests at 10 atm were used to determine the thermal and diffusional effects of high-pressure helium gas on the reaction of H_2O and CO_2 with the superoxide materials. These high-pressure tests provided an indication of the hyperbaric performance of the superoxide mixtures in comparison to commercial purity KO_2.

EXPERIMENTAL METHODS

Reactor Design Criteria

The reactor used in the tests described below was designed on the basis of the following criteria:

1. A small sample size must be used. This criterion was necessary because $Ca(O_2)_2$ is not commercially available; therefore, it must be prepared on a laboratory scale in modest quantities (i.e., ~5-20 g per run). This limitation in the quantity of $Ca(O_2)_2$ for use in preparing $KO_2/Ca(O_2)_2$ mixture samples mandated a small reactor since it was not desirable to spend a large amount of time and resources on the synthesis of $Ca(O_2)_2$.

2. The superoxide granule/pellet size should be comparable to that in commercially available superoxide breathing device canisters. Since one goal of the program was to improve upon the utilization efficiency of commercial KO_2, it seemed appropriate to test granules or pellets of superoxide mixtures that were in the same size range as those which are found in existing KO_2-based devices. In this way, a more accurate assessment could be made of whether the mixtures would exhibit improved reaction performance in an actual breathing apparatus canister.

3. The test pressure should range from 1 to 10 atm. In earlier work, superoxide mixtures had given superior performance to KO_2 in tests conducted at 1 atm (ref. 13). A major goal of this work was to determine whether the improvement in reaction performance was also seen at hyperbaric pressures of up to 10 atm.

4. The reaction temperature should range from 0 to 200°C. If initial testing at 40°C showed a significant improvement in hyperbaric reaction performance for the superoxide mixtures, then further tests would be conducted at lower and higher temperatures. In a diving apparatus used in Arctic waters, the superoxide granules or tablets could be exposed to temperatures as low as 0°C. Temperatures as high as 360°C have been observed near the center of a reacting KO_2 bed in atmospheric-pressure breathing apparatus (ref. 11). However, since it seemed likely that the temperature of a reacting superoxide bed in a diving apparatus would be moderated

somewhat by the hyperbaric helium, 200°C was chosen as the upper temperature bound in the design temperature range.

The reactor which was designed and fabricated based on these criteria is shown in figure 1. A choice was made to test single pellets of superoxides to meet both criteria Nos. 1 and 2. The pellet size was based on the KO_2 tablets used in the Drager model "Oxy SR 60B," 60-min emergency breathing device and the KO_2 granules used in the MSA 60-min emergency breathing device (part number 464213) (refs. 8 and 13). The tablets from the Drager device were 9-mm diam and had a maximum thickness of 4.6 mm. The granules from the MSA device were irregular in size and shape, but fell within a range of ~3-10 mm in the largest dimensions. Figure 2 compares the 9.52-mm diam pellets fabricated here with the two commercial KO_2 forms. Two pellet die sizes were available for use; a 6.35-mm (0.25-in.) i.d. (i.d. = inside diam) die, and a 9.52-mm (0.375-in.) i.d. die. A decision was made to design the reactor cavity based on the larger 9.52-mm diam pellet size since it would be closer to the commercial 9-mm-diam tablets. Although the overall dimensions of the pellets were close to those of the commercial KO_2 tablets and granules, the slightly larger dimensions and high density of the pellets resulted in the pellets being heavier than the commercial forms. Since the fabricated pellets had nearly twice the mass as the commercial KO_2 forms, the pellets would be expected to exhibit the poorest utilization efficiency of the three superoxide forms, since the diffusional resistance for reactant gases moving to the center of the pellet would be greater because of a greater diffusion barrier thickness.

Figures 3(a)-3(c) are cutaway drawings of the reactor interior. Figure 3(a) shows an enlarged view of the reactor cavity with a pellet in place on the 0.31-mm o.d. (o.d. = outside diam) (30-gauge) hypodermic-needle thermocouple probe (copper/constantan, type T). The stainless-steel-sheathed thermocouple probe was the only point of contact of the pellet with the reactor. Figures 3(b) and 3(c) show cross sections of the empty reactor, with the cross sections made through the inlet- and outlet-gas flow paths, respectively. The inlet test-gas stream was split in two inside the reactor and entered perpendicular to each face of the cylindrical pellet (fig. 3(b)). It then flowed radially outward and over the edges of the pellet, and left the reactor through the 10-μm pores of a cylindrical, stainless-steel frit located at the equator of the pellet (fig. 3(c)). An annular space behind the frit distributed the gas evenly to four exit drillings which joined together at the top of the reactor. Figures 4(a)-4(c) are photographs that show the interior of the reactor. The reactor was machined from type 304 stainless steel and was sealed with Viton O-rings so that the reactor could be used over the design range of 0-200°C. Figure 4(a) shows the annular space behind the 10-μm frit and the hypodermic needle probe. Figure 4(b) shows the lower portion of the reactor with a pellet mounted in place. Figure 4(c) shows the upper and lower portions of the reactor.

Although the reactor was designed specifically for testing the custom pellets of KO_2 or $KO_2/Ca(O_2)_2$, it could also be used to test granules or tablets of KO_2 from commercial portable breathing apparatus by mounting the samples on the thermocouple probe. After the KO_2 and $KO_2/Ca(O_2)_2$ superoxide mixture pellets had been tested at 10 atm it seemed desirable to test the commercial granules and tablets under similar conditions. In this way it could be determined whether the laboratory pellet fabrication carried out in this work resulted in materials that were dramatically inferior with respect to porosity when compared to commercially fabricated materials. Lower porosity would be indicated by poorer reaction of the materials caused by their inherently inferior mass-transfer characteristics.

Flow-System Test Facility

Figure 5 is a schematic of the Flow-System Test Facility, which was assembled to test the reactivities of superoxides with CO_2 and H_2O. The flow system was of the single-pass type (ref. 26). Dry test gas of constant, known composition entered the system and was humidified by passage through a gas bubbler before entering the reactor and flowing around the superoxide sample. The chemical composition of the gas leaving the reactor was measured before it was vented from the system. Since the composition, pressure, and flow rate of the gas entering and leaving the reactor were known, the amounts of CO_2 and H_2O being absorbed and the amount of O_2 being evolved by the superoxide sample could be determined.

In all the tests described here, the superoxide sample was contained in the stainless-steel reactor described previously. The thermal environment of the reactor could be varied by immersing it in a constant temperature bath with a temperature range of 0 to 200°C. However, in all the tests except one, the reactor temperature was in the range of 39.2-39.6°C. In the one other test, the reactor temperature was 60.3°C.

Humidification of the test gas entering the reactor was accomplished by flowing the dry test gas through a stainless-steel, glass-lined gas bubbler, which was partially filled with distilled water and immersed in a constant temperature bath set to the desired dew point. A packing of glass wool above the surface of the distilled water inside the bubbler prevented the entrainment of water droplets or mist in the gas stream and also aids in saturating inlet gases. With this humidification system, the dew point of the gas leaving the humidifier was assumed to be the temperature of a platinum resistance thermometer immersed in the constant temperature bath. This assumption was checked by measuring the dew point of the gas with a humidity analyzer during the flow-system calibration procedure to be described. The capability of bypassing a portion of the inlet flow around the humidifier was also built into the system, but this capability was not needed over the inlet dew-point range tested here. To prevent condensation of moisture in the flow system when the dew point of the test gas was above ambient temperature, all of the parts of the flow system exposed to H_2O were enclosed in a constant temperature oven set to 40.0 ±0.5°C.

The flow rates of the test gas entering the humidifier and the gas analyzers were measured and controlled by mass flow controllers (model 1259, MKS Instruments, Inc., Burlington, MA). The flow of test gas downstream from the reactor was split into two streams: an analyzed stream and a bypass stream. In all the tests made here the flow rate to the analyzers was maintained at 200 SCCM (standard cubic centimeters per minute at 1 atm and 273 K). During the high-pressure tests, the majority of gas went into the bypass stream. The pressure in the reactor was maintained to within ±0.01 atm via the bypass stream using a back-pressure regulator (model 10, 0-10.2-atm gauge (0-150-psig) range, Fairchild Industrial Products Company, Winston-Salem, NC). The pressure drop for the analyzed portion of the gas stream was across the control valve of the 0-500-SCCM mass-flow controller. The flow rate of the bypass stream was measured using a mass flowmeter (Matheson Gas Products Inc., Newark, CA).

In all the tests described here, premixed test gases were used, although custom blends of helium and CO_2 could also be made using another mass flow controller connected to a supply of CO_2. Since the mass flowmeters and flow controllers were factory calibrated for nitrogen or air, real flow-rate values were calculated from the mass-flowmeter or flow-controller output signals using correction factors which were calculated on the basis of the known composition (e.g., dry input gases) or real-time-measured composition of the gas stream. The correction factors were calculated based on the heat capacities of the components of the gas mixture.

The composition of the gas downstream from the reactor was determined using a model S-3A, N-22n oxygen analyzer (Applied Electrochemistry Co., Sunnyvale, CA), a model AR-500R infrared carbon dioxide analyzer (Anarad Inc., Santa Barbara, CA) and a model 911 Dew-All digital humidity analyzer (E.G. and G. Inc., Waltham, MA). The barometric pressure, as well as the pressures at the humidifier, reactor, humidity analyzer, and gas analyzers (CO_2 and O_2), were measured with capacitance manometers of the appropriate range (models 310-BAS-1000, 400-101-SP, 220-BH-10000, 400-100-SP, and 220-AH-100, respectively, MKS Instruments, Burlington, MA). The lines connecting the various components of the flow system were 1.75- and 4.57-mm-i.d. stainless-steel tubing.

Data acquisition and reduction were accomplished using an HP 9816S desk-top computer interfaced with an HP 3495A 40 channel scanner and an HP 3455A digital voltmeter (from Hewlett Packard, Palo Alto, CA). The analog outputs of all of the analyzers, probes, manometers, flowmeters, and sensors were connected to the scanner with shielded signal cable. During the flow test, a real-time plot of some of the data was displayed on the video monitor of the 9816S computer. In addition, portions of the calibration and test procedure were automated by means of an HP 3497A controller connected to 40 high-voltage actuators. These actuators opened and closed solenoid valves to admit the various gases and direct the course of the gas flow through the system.

Superoxide Pellet Fabrication

The pellets were made by compressing 1.2 cm^3 portions of the appropriate superoxide powder (<0.038-mm-diam particles) in a modified Parr pellet press (Parr Instrument Co., Moline, IL), using a 9.52-mm- (3/8-in.)-diam punch and die. The uniform volume (1.2 cm^3) of the appropriate superoxide powder was obtained by striking off the powder level in a stainless-steel measuring spoon. The pressing operation was carried out inside a dry glove box (Vacuum Atmospheres Co., Hawthorne, CA). Before ejecting the pellet from the die, a 0.33-mm diam hole (for mounting the pellet on the thermocouple probe) was drilled into the pellet using the specially made hand drill shown in figures 6(a) and 6(b). The drill was also used to drill holes in the KO_2 granules and tablets. The granules usually had to be trimmed to fit into the die for drilling.

Flow-Test Procedure

All of the tests described in this report were carried out at a volumetric flow rate of 326 ±17 cm^3/min. This volumetric flow rate at the reactor pressure and temperature conditions gave measurable depletion in the concentration of CO_2 downstream of the superoxide sample. The mass flow rate was 300 SCCM for 1-atm tests whereas the mass flow rate had to be 3000 SCCM for 10-atm tests to obtain a volumetric flow rate at pressure of 326 cm^3/min. In the case of the laboratory fabricated pellets, a volumetric flow rate of 326 cm^3/min gave space velocities over the pellet surfaces of ~3.0-3.8 cm/sec which was within the range expected for tablets or granules inside a canister used for hyperbaric breathing applications. However, the space velocity range of the test gas over the KO_2 tablets and granules was significantly lower than that for the pellets since the commercial KO_2 forms displaced less of the reactor cavity volume than the pellets. Because of the more complex shapes of the commercial KO_2 forms, it was not possible to calculate the flow rate required to give the same space velocities over the tablets and granules. Therefore, it was decided to test the commercial KO_2 at the same volumetric flow rate as the pellets.

After the test sample was weighed, it was loaded into the reactor under the dry nitrogen atmosphere of the glove box. Immediately before a flow test, the oxygen and carbon dioxide analyzers were calibrated by measuring their response to each of eight dry, primary-standard gas mixtures. The calibration procedure was carried out by following the prompts of a custom computer program and the responses of the analyzers were stored by the computer for later use during the real-time data reduction.

In the last part of the calibration procedure, the flow system (including the lines leading up to the valves on the reactor) was evacuated and back filled with dry zero gas (i.e., the diluent gas which was used to make up the CO_2 test-gas mixture). In one of the tests, the zero gas was nitrogen but in the remaining tests helium was used. With the flow system at test pressure, the reactor was purged with zero gas. Then with the reactor bypassed, the flow system was evacuated, back filled with dry test gas (5.0% CO_2 in helium for 1-atm tests and 0.50% CO_2 in helium for 10-atm tests) and equilibrated with moisture at the test pressure by directing the gas stream through the humidifier. The test was initiated by a command to the computer which then opened the appropriate solenoid valves after 100 sec of baseline data were collected. The solenoid valves directed the humidified test gas through the reactor.

In all of the tests described here, the superoxide sample was reacted with humidified test gas for 1.5 ksec, and then, with the reactor bypassed, the flow system was purged with dry zero gas. Once most of the CO_2 and H_2O had been flushed from the system, the reactor was purged with the dry zero gas and brought to atmospheric pressure (if necessary). In all but two of the tests, the sample was removed from the reactor and a visual examination was made of the exterior of the sample. Then the sample was cut in half to observe the thickness of the product layer. For two of the hyperbaric tests, the sample was left in the reactor after reaction at 10 atm and the flow system was purged with the test gas used in the 1-atm tests. After equilibrating the flow system with moisture at 1 atm, the samples were reacted for an additional 1.5 ksec before they were removed from the reactor for visual examination.

Tables 1 and 2 list the chemical composition and physical characteristics of the laboratory-fabricated superoxide pellets and the commercial KO_2 samples, respectively. Tables 3 and 4 summarize the flow-system test facility reaction conditions for the superoxide pellet samples and the commercial KO_2 samples, respectively.

RESULTS

Expression of Rate Data

Since the volumetric flow rates (at test pressure) were essentially the same for all the tests (i.e., ~326 cm^3/min), the rates of O_2 evolution and CO_2 absorption were expressed simply in terms of the μmol of gas absorbed or evolved per second, without normalization to a unit volume flowing through the reactor. Tables 5 and 6 list the rates of O_2 evolution and CO_2 absorption for the laboratory-fabricated pellets of KO_2 and $KO_2/Ca(O_2)_2$ mixtures and the commercial granules and tablets of KO_2, respectively. Both tables give maximum rates and average rates. In table 5, the maximum rates are expressed in two ways: μmol s^{-1} and μmol s^{-1} cm^{-2}. The latter expression of the rates for the pellets accounts for the slight difference in the size of the pellets and hence the surface area of superoxide which was initially exposed to the test gas. The initial surface areas of the pellet samples are given in table 1. It was assumed that the maximum rates of O_2 evolution and CO_2 absorption would occur when the amount of surface of superoxide exposed to the test gas was at a maximum, that is, near the beginning of the test before a significant thickness of product coating built up. The surface of superoxide exposed was assumed to be approximated by the geometric surface area of the pellet. Therefore, dividing the maximum rates by the geometric surface area of the pellet normalized the rates to a unit square centimeter of superoxide surface exposed to reactants. In the case of the rates for the granules and tablets given in table 6, the initial surface of superoxide exposed to the reactants was not easily determined and so no normalization of the rates to unit surface area was performed.

The average rates given in tables 5 and 6 were calculated by dividing the total amounts of O_2 evolved and CO_2 absorbed by the reaction time (1.5 ksec). The average rates are expressed in μmol s^{-1} for comparison with the maximum rate values, and in μmol s^{-1} g^{-1} so that the smaller commercial tablets and granules could be compared to the larger, laboratory-fabricated pellets.

Extent of Utilization Data

The amounts of O_2 evolved and CO_2 absorbed by the superoxide pellets and the commercial granules and tablets are listed in tables 7 and 8, respectively. The CO_2 absorption data were not expressed in terms of percentages of the CO_2 capacities of the samples because those CO_2 capacities vary depending on whether K_2CO_3 or $KHCO_3$ is the CO_2 reaction product.

Physical Characteristics of the Superoxide Samples

Tables 9 and 10 summarize the observations which were made of the physical state of the superoxide pellets and of the KO_2 tablets and granules, respectively, after reaction with humidified CO_2. An evaluation was made of (1) the change (if any) in the shape of the sample as a result of reaction, (2) the consistency of the product coating, and (3) the thickness of the product coating. In the majority of the samples, a large unreacted core of superoxide existed beneath the outside product coating. The most desirable product coating is one that is highly permeable to reactant gases so that utilization of the superoxide in the interior of the sample is high and at the same time is hard so that fusion of the pellets, granules or tablets in a canister of the superoxide would be minimized. With this kind of coating, the utilization of a bed of the superoxide would not be hampered by particles in the bed fusing together, and hence being bypassed by the gas flow. Also, the reuse of canisters would be possible, since the spent superoxide material could be poured from the canister if the product coating was hard and nonfusible.

Temperature Data

The maximum temperatures which were observed during the reaction of the superoxide pellets and the commercial KO_2 tablets and granules with humidified CO_2 are listed in tables 11 and 12, respectively. The temperatures were measured near the center of the samples and probably do not accurately reflect surface temperatures, which could have been significantly higher than those listed.

DISCUSSION

Low-Pressure (1-atm) Tests

Potassium superoxide pellets- A series of tests was run in which the ratio of the inlet H_2O to CO_2 was varied from 1.13 to 0. This series included test Nos. KS-2, KS-5, KS-6, and KS-9. Figure 7 compares the rates of O_2 evolution and the amount of O_2 evolved as a function of reaction time for the series of tests. Figure 8 is a similar plot of the rates of CO_2 absorption and the amounts of CO_2 absorbed during the same tests as a function of reaction time. The spikes on the rate of CO_2 absorption traces in figure 8 and later figures are the result of electronic noise in the infrared CO_2 analyzer.

Several trends are apparent in the series of tests:

1. Rates. As the inlet H_2O/CO_2 ratio increased, the decay in the rates of O_2 evolution and CO_2 absorption from the peak rate values was more rapid. This trend in the decay of the maximum rates suggests that the product coating which was formed with the higher H_2O/CO_2 ratios was less permeable to reactant gases than that formed with lower ratios. In test No. KS-2, the rate leveled off and actually increased in the last half of the test. This behavior was caused by the soft, mushy consistency of the coating which allowed fresh areas of the inner pellet to be exposed when the swelling of the pellet created cracks in the soft crust. As a result of the cracks, the initial low permeability of the product coating was somewhat overcome.

2. Utilization. As the inlet H_2O/CO_2 ratio was increased, the utilization of the superoxide sample (in terms of the amounts of O_2 evolved and CO_2 absorbed) decreased. This trend toward lower utilization was also consistent with the formation of a less permeable product coating at high H_2O/CO_2 ratios.

3. Physical Characteristics. As the H_2O/CO_2 ratio was increased, the product coatings became soft in consistency (table 9). The soft, mushy consistency of the coatings was characteristic of a product made up principally of highly hydrated potassium hydroxide (i.e., $KOH \cdot nH_2O$, $n > 2$) and K_2CO_3.

4. Thermal Effects. The peak temperatures for the three tests with H_2O/CO_2 ratios greater than zero was approximately the same (table 11). This uniformity in sample temperatures was consistent with the fact that all three of these tests had maximal rates of O_2 evolution and CO_2 absorption of similar magnitude.

In test No. KS-9, an extreme case was tested in which the inlet H_2O/CO_2 ratio was 0 (the gas stream was not humidified). For this test initially CO_2 reacted with KOH impurity in the sample. This $KOH-CO_2$ reaction resulted in the absorption of CO_2 and the release of H_2O. The released H_2O could then diffuse into the sample and react with KO_2 to produce additional KOH and O_2. For a fuller explanation of this dry CO_2-KO_2 reaction behavior, see reference 13. The lower overall reactivity exhibited by the sample in this test was the consequence of the limited amount of KOH initially available for reaction (~10-15 weight % of sample), and of the gradual removal of product H_2O via transfer to the gas stream and through production of K_2CO_3 hydrates. Since H_2O was the necessary ingredient for the reaction of KO_2 with CO_2, as the H_2O was removed, no additional KOH was formed and the reaction became starved for H_2O. It is interesting to note, however, that the CO_2-scrubbing capacity exhibited by the sample in test No. KS-9 was superior to that for No. KS-2 which had the highest inlet H_2O concentration (fig. 8(b)). This series of tests indicated that high inlet H_2O/CO_2 ratios are detrimental to CO_2 absorption.

The best overall reaction performance in the series of KO_2 pellet tests was exhibited by the sample reacted with an H_2O/CO_2 ratio of 0.42 (test No. KS-6). It had the highest sustained rates of O_2 evolution and CO_2 absorption, the largest amounts of O_2 evolved and CO_2 absorbed as well as a hard but apparently more porous product coating. The reaction behavior of the KO_2 in this series of tests was consistent with earlier work carried out at Ames (ref. 24).

Test No. KS-1 was conducted in order to compare the reaction performance of a KO_2 sample reacted with humidified CO_2 in a nitrogen atmosphere with that of a similar sample reacted in a helium atmosphere (test No. KS-2). For test Nos. KS-1 and KS-2, the reaction conditions were identical except for the diluent used in the test gas mixtures (nitrogen and helium, respectively). Under these similar conditions, the overall reaction performance was better for the sample tested in a helium atmosphere although both samples exhibited O_2 utilization efficiencies below 50% (table 7). Perhaps the most dramatic difference between the two tests was seen in the maximum sample temperatures recorded during the reactions (table 11). The maximum sample temperature was nearly 10°C higher for the sample reacted in nitrogen. Since the rates of O_2 evolution and CO_2 absorption were fairly similar between the two tests, the lower sample temperature for test No. KS-2 can probably be attributed to the higher thermal conductivity of the flowing helium stream which removed the exothermic heat of reaction more efficiently.

<u>Commercial potassium superoxide tablets and granules</u>- A series of flow tests was carried out on KO_2 samples taken from commercial breathing canisters so that the reaction performance of the commercially formulated KO_2 could be compared with the performance of the laboratory fabricated pellets. The pellets of KO_2 mentioned above had been fabricated from powder obtained by grinding the commercial KO_2 granules. Therefore, by testing the granules, it was possible to evaluate the effect that pellet fabrication had on the reaction performance of the KO_2. It was postulated that pelletizing the KO_2 would result in a sample with lower porosity than the commercial granule.

The KO_2 tablets which were tested here contained trace amounts of a catalyst which enhanced the release of O_2 by catalyzing the decomposition of hydrogen peroxide (a low-temperature KO_2-H_2O reaction intermediate). The catalyst is probably more important at lower reaction temperatures (<50°C) where hydrogen peroxide would be thermally stable.

The same general trends of reaction performance in response to changes in inlet H_2O/CO_2 ratios which were observed for the KO_2 pellets were also seen for the commercial tablets and granules. In test Nos. KS-10 and KS-12, KO_2 tablets were reacted with test gas having an H_2O/CO_2 ratio of 1.14 and 0.56, respectively. Figure 9 compares the rates of O_2 evolution and the rates of CO_2 absorption as a function of reaction time for these KO_2 tablet tests. KO_2 granules were reacted in a similar manner to the tablets in test Nos. KS-11 and KS-14, and figure 10 shows plots of the rates of O_2 evolution and CO_2 absorption for the granule tests.

As was the case in the series of pellet tests, the decay in the rates of O_2 evolution and CO_2 absorption was more rapid with the higher inlet H_2O/CO_2 ratio. Also, the release of the available O_2 and the CO_2-scrubbing capacity were greater with the lower H_2O/CO_2 ratio.

When the results for laboratory fabricated pellets (test Nos. KS-2 and KS-5 (tables 5 and 7)) are compared with those for the commercial KO_2 (test Nos. KS-10 through KS-12 and KS-14 (tables 6 and 8)) a number of general trends become apparent.

1. Rates. Since the KO_2 pellets had over twice the mass as the commercial tablets and granules, it is best to compare the average rates of O_2 evolution and CO_2 absorption which have been normalized with respect to sample weight (i.e., $\mu mol\ s^{-1}\ g^{-1}$). This normalization to sample mass makes some allowance for the larger surface initially exposed to the reactant gas by the pellets since the densities of the three KO_2 forms are similar.

Both commercial forms of KO_2 exhibited superior average rates of O_2 evolution and CO_2 absorption when compared to KO_2 pellets which were tested under similar inlet pH_2O conditions (compare test No. KS-2 with Nos. KS-10 and KS-11, and test No. KS-5 with Nos. KS-12 and KS-14). It is especially interesting to compare test Nos. KS-2 and KS-5 with Nos. KS-11 and KS-14, since the pellets in the former two tests were fabricated out of powder derived from ground up granules similar to those used in the latter two tests. While it is true that there was some loss in the purity of the KO_2 during the pellet fabrication process,[1] the decrease in purity was not significant enough to explain the differences in the rates of O_2 evolution and CO_2 absorption. The lower rates exhibited by the pellets suggests that the pellets are not as porous as the commercial materials. This lower porosity may be a function of the pellet fabrication pressure or the size range and/or size distribution of the feed-powder particles. The lower porosity would tend to decrease the diffusion of H_2O and CO_2 into the interior of the pellet.

2. Utilization. The commercial forms of KO_2 were also more highly utilized than the KO_2 pellets during the tests carried out under similar conditions. In the case of the tablets, the presence of the catalyst apparently resulted in all the O_2 being released, even though the CO_2 scrubbing capacity was rather modest.

Potassium superoxide/calcium superoxide pellets- Two $KO_2/Ca(O_2)_2$ mixture formulations were tested in which the amount of $Ca(O_2)_2$-containing powder added to the KO_2 powder consisted of 25% and 50% of the final weight of the mixture. Actually, each superoxide component of the binary mixture was itself a mixture of the superoxide species plus impurities present from the original synthesis of the superoxide or from subsequent contamination. The KO_2 powder contained up to [illegible]% KOH, K_2CO_3 and $KHCO_3$, whereas the $Ca(O_2)_2$ also contained CaO_2, $Ca(OH)_2$, and traces of $CaCO_3$. For example, when mention is made of a 76%/24% $KO_2/Ca(O_2)_2$ mixture, the percentage values refer to the weight of KO_2 including impurities, mixed with the weight of $Ca(O_2)_2$ including its impurities.

It was decided that the comparison of the reaction performance of the $KO_2/Ca(O_2)_2$ mixtures with that of KO_2 should be made under the highest inlet pH_2O conditions that could be seen in a portable breathing device, that is, at 47 mm Hg (dew point = 37°C). Earlier testing of small granules of a 75% KO_2, 25% $Ca(O_2)_2$ mixture at inlet dew points of -25°C had indicated that the mixture dramatically

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[1] The purity of the KO_2 decreased from 90.7 to 86.5% probably because traces of H_2O in the glove box atmosphere reacted with the high KO_2 surface area presented by the finely ground powder.

outperformed KO_2 granules formulated under identical conditions with respect to reaction rates and utilization efficiency (ref. 13).

Comparison of Rates: Figure 11 shows plots of rates of O_2 evolution and CO_2 absorption observed during the course of test Nos. KS-2, KS/CaS-1, and KS/CaS-3 which were carried out at 1-atm pressure with an inlet dew point of -37°C. The plots clearly show that the two mixture formulations exhibited superior reactivity since the maximum rates of O_2 evolution and CO_2 absorption did not decay as rapidly for the mixtures as for the KO_2 pellet. Of the two mixtures, the 76%/24% $KO_2/Ca(O_2)_2$ formulation had the superior reaction performance with regard to maximum rates of O_2 evolution. The higher sustained rates of reaction for the mixture pellets are also reflected in the higher maximum temperatures which are listed in table 11.

Comparison of Utilization: The higher sustained rates of O_2 evolution and CO_2 absorption of the mixtures also resulted in higher utilization of the available O_2 and CO_2-scrubbing capacity. Figure 12 shows plots of the amounts of O_2 evolved and CO_2 absorbed as a function of reaction time for the three tests. Two times the amount of O_2 was evolved and ~3.5 times the amount of CO_2 was absorbed by the mixture pellets when compared to the KO_2 pellet tested under identical conditions. The two superoxide mixture pellets also exhibited superior utilization efficiency when compared with the KO_2 pellet reacted under the optimum inlet dew point of -20°C (table 7, test No. KS-6). Of the two mixtures, the 76%/24% $KO_2/Ca(O_2)_2$ pellet exhibited the highest utilization efficiency.

Comparison of Physical Characteristics: Perhaps the most dramatic difference between the $KO_2/Ca(O_2)_2$ pellets and the KO_2 pellet from tests with an inlet dew point of 37°C was the nature of the product coating. Whereas the KO_2 pellet was swollen with a soft, mushy, bubbly coating, the $KO_2/Ca(O_2)_2$ pellets were unchanged in shape and dimension from the start of the test, and had a very hard coating. The KO_2 pellets reacted under lower inlet dew points (i.e., -25°C for test No. KS-5 and -20°C for test No. KS-6) also had harder coatings than the KO_2 pellet in the high dew point test (No. KS-2). However, earlier work with KO_2 granules reacted at dew points of -25°C (ref. 13) showed that the granules were fused to one another and stuck to the reactor walls, whereas granules consisting of a 76%/24% $KO_2/Ca(O_2)_2$ mixture did not fuse together, were free flowing after reaction and could be poured out of the reactor. The advantage of the nonfusing nature of the $KO_2/Ca(O_2)_2$ mixture over the fusibility of KO_2 would be especially attractive in applications where the breathing canister would be recycled by removing spent material and refilling it with fresh superoxide.

It was postulated that when the $Ca(O_2)_2$ was mixed with the KO_2 powder it acted as an O_2-producing, CO_2-absorbing, nonfusing desiccant which tied up excess H_2O and prevented the formation of a low-melting, hydrated-hydroxide/carbonate coating on the reacting surface of the pellet. In the case of the superoxide mixtures, a coating was formed which consisted of a mixture of $K_2CO_3 \cdot 3/2H_2O$, $K_2CO_3 \cdot 1/2H_2O$, $KHCO_3$, and $CaCO_3$ and which apparently was more permeable to reactant gases than a fused, highly hydrated hydroxide/carbonate coating. The hydrated hydroxide/carbonate coating was postulated to impede further reaction of the sample by bonding with reactant H_2O in a hydration layer which then reduced the migration of H_2O and CO_2 to the unreacted KO_2 surface.

High-Pressure (10-atm) Tests

The reaction behavior of all of the superoxide samples during reaction with humidified CO_2 in helium at 10-atm total pressure was dramatically different than that seen at 1 atm. Figures 13-17 are plots of the rates of O_2 evolution and rates of CO_2 absorption as a function of reaction time for each of five 1|10-atm flow-test sample pairs: KS-2|KS-3, KS/CaS-1|KS/CaS-2, KS/CaS-3|KS/CaS-4, KS-6|KS-7, and KS-14|KS-16. From this set of plots, it can be seen that the maximum rates of O_2 release and CO_2 absorption seen during the 10-atm flow tests are significantly lower than during the comparable 1-atm tests. This drop in reactivity at 10 atm was seen for KO_2 pellets, commercial KO_2 granules and tablets, and $KO_2/Ca(O_2)_2$ mixture pellets and was somewhat independent of inlet pH_2O. Although, with the exception of the $KO_2/Ca(O_2)_2$ pellets, more significant relative drops in reactivity were seen with sample pairs tested with an inlet pH_2O of 17-24 mm Hg.

In general, from tables 7 and 8 it is apparent that the decrease in reaction rates at 10 atm was accompanied by reduced utilization of the superoxide samples. The only exception to this reduced utilization was found in the sample pairs evaluated in test Nos. KS-2 and KS-4, in which the amount of O_2 evolved at 10 atm was slightly higher than at 1 atm. The CO_2 absorption for the same sample pairs was reduced by a factor of 1.2 to 1.5 in going from 1 to 10 atm. For all of the other 1|10-atm sample pairs, the decline in overall reaction performance was much more dramatic. In general, the CO_2 absorption was affected more than the O_2 evolution by the increased reaction pressure. A similar decrease in the overall efficiency of CO_2 absorbents at hyperbaric pressure has also been documented (refs. 27 and 28). Interestingly, the reaction conditions which gave the best performance at 1 atm resulted in the most serious decline in performance at 10 atm. For example, the KO_2 pellet in test No. KS-6 exhibited 50% greater O_2 evolution and 150% greater CO_2 absorption than the pellet in test No. KS-2; yet the corresponding sample evaluated at 10 atm under identical conditions in test No. KS-7 exhibited about one-third of the O_2 evolution and slightly less CO_2 absorption compared to test Nos. KS-3 and KS-4.

There are several possible causes for the decline in reaction performance observed for the samples tested at 10 atm compared to their 1-atm counterparts. Each of these possible causes will be considered in the following paragraphs.

Thermal effects- It is possible that thermal quenching or moderation of the exothermic KO_2-H_2O and KOH-CO_2 reactions by the high heat capacity, 10-atm helium stream resulted in lower O_2 evolution and CO_2 absorption rates than in the tests at 1 atm. It is apparent from tables 11 and 12 that the temperatures of the cores of the superoxide samples in the 10-atm tests were at the most only 1-2°C above the reactor temperature, and were dramatically lower than the 5.7 to17.1°C temperature rises seen during the 1-atm tests. Although these lower temperatures could be the result of thermal quenching, it is also possible that the reactivity of the sample was low (for some other nonthermal reason); therefore, not as much heat was generated.

An attempt was made to determine if lower sample temperature was a factor in the lower reaction performance observed during the 10-atm tests. In test No. KS-8, the initial reactor temperature was raised to 60.3°C, a temperature which was slightly higher than the highest recorded sample temperature of pellets tested at 1 atm. From the data for this test (tables 5 and 7), it is apparent that a significant improvement was made in the reaction performance by raising the initial sample temperature 20°C from that used in test No. KS-7. But the reaction performance was still far below that of the sample in the corresponding 1-atm test (No. KS-6). It is possible that the pellet surface temperature in test No. KS-6 was significantly higher than the 47°C recorded core temperature, in which case, it would have been necessary to react the pellet at a higher core temperature in test No. KS-8 to give an adequate thermal simulation of the sample in test No. KS-6. However, on the basis of the results in test Nos. KS-6 through KS-8, it appears that thermal quenching was not the sole cause of the lower reaction performance of the samples tested at 10 atm.

Sample porosity- After the 10-atm tests of the laboratory-fabricated pellets, it was initially postulated that the poor reaction performance could be an artifact caused by the lower porosity of the pellets compared with commercial KO_2 formulations. Presumably, the commercial KO_2 forms would not exhibit such a dramatic drop off in reactivity at the higher pressure of 10 atm. However, when the commercial KO_2 tablets and granules were tested, the reduction in reactivity at 10 atm was equal to or greater than the reduction seen for the pellets. If the porosity of the pellets was lower than that of the KO_2 tablets or granules, then porosity does not seem to be a significant factor in determining the reactivity of the samples at 10 atm.

Bulk-diffusivity effects- For binary gas mixtures at pressures below 10 atm, the diffusion coefficient is inversely proportional to the pressure, increases with increasing temperature, and is almost independent of composition for a given gas pair (ref. 29). Table 13 lists the diffusivities of CO_2 and H_2O in helium over a temperature range of 10 to 120°C (283-393 K) and at absolute pressures of 1 and 10 atm. The diffusivities for CO_2 and H_2O listed in table 13 were obtained by performing a least squares, linear regression analysis of the experimentally determined values given in reference 30. The diffusivity values listed for 10 atm were obtained by merely dividing the 1-atm values by 10. It is interesting to note that the diffusivity of H_2O in helium at 40°C is 1.4 times higher than that of CO_2. In light of what has been said above about the effect of inlet H_2O/CO_2 concentration ratios on the reaction performance of KO_2, it seems that the greater diffusivity of H_2O in helium to that of CO_2 would also tend to favor the formation of hydrated hydroxide/carbonate coatings over hydrated carbonate coatings.

If bulk diffusivity effects alone were the cause of the decline in the reaction performance seen as the pressure was increased from 1 to 10 atm, then at first one would expect that the maximum rates of O_2 evolution and CO_2 absorption seen at 10 atm would be only about one-tenth that seen at 1 atm. However, this was not the case. The maximum rates of O_2 evolution and CO_2 absorption at 10 atm are one-third to one-fifth those at 1 atm. These higher than expected rates at 10 atm suggest that the reactions at 1 atm were probably already mass-transfer limited because of factors not related to the bulk diffusivity. For example, no flow tests at high space velocities were conducted in the work described here, and it is possible that higher initial rates of O_2 evolution and CO_2 absorption at 1 atm would be seen at higher space velocities. Assuming that the rates of O_2 evolution and CO_2 absorption did not increase for 10-atm tests at a similarly higher space velocity, then the expected factor of 10 difference between 1-atm and 10-atm rates would be observed.

It seemed reasonable that if the bulk diffusivity was a major cause of the overall drop in reaction performance for the tests at 10 atm, then it should be possible to restore the reaction performance of a superoxide sample which had been tested at 10 atm by lowering the pressure to 1 atm and continuing the test. This reaction scheme was carried out on the samples reacted during test Nos. KS/CaS-5 and KS-16. The samples were tested at 10 atm for 1.5 ksec, and then reactor and sample were rapidly purged with dry helium to remove remaining moisture and CO_2. Next the pressure was lowered to 1 atm and with the reactor bypassed, the flow system was equilibrated with test gas under similar inlet pH_2O, pCO_2 and volumetric flow rate conditions as the 10-atm portion of the test. Finally, the test was continued for an additional 1.5 ksec at 1 atm. Since the utilization of the samples was very poor at 10 atm, most of the sample remained for the second, 1-atm stage of the test. The 1-atm portion of the tests was then compared to that of a 1-atm test conducted on a similar sample (test No. KS/CaS-3 for the $KO_2/Ca(O_2)_2$ sample and test No. KS-14 for the KO_2 granule sample). The results of the comparisons are shown in table 14. The values in table 14 were calculated as follows. The sample pair reacted during test Nos. KS-14 and KS-16 is used below as an example.

1. The volume of O_2 evolved per gram of sample during the 10-atm portion of test No. KS-16 was added to the volume of O_2 which was produced by the sample in the sealed reactor during the time it took to equilibrate the flow system to 1-atm reaction conditions. The latter volume of O_2 was due to the slow reaction of the unreacted core of the sample with moisture contained in the product coating, and once the reactor was again opened to the flow system (at the start of the 1 atm phase of the test) the O_2 was purged out of the reactor and appeared as a spike on the O_2 evolution rate versus reaction time trace. During the equilibration time, the sample did not react with CO_2 since the residual CO_2 in the reactor had been purged with helium.

2. The volume of O_2 evolved by the sample during reaction at 10 atm and during the equilibration period was then used to determine the point in time during test No. KS-14 (the comparable 1-atm test) when the same amount of O_2 had been evolved. This determination was done graphically using a plot of O_2 evolved per gram of sample as a function of reaction time for test No. KS-14.

3. Next, the instantaneous rates of O_2 evolution and CO_2 absorption at the point in time determined in step No. 2 were taken from the plots of the rate of O_2 evolution and rate of CO_2 absorption as a function of reaction time for test No. KS-14. These rates were used as the expected rates for the 1-atm test phase of

test No. KS-16. In making the determinations, it was assumed that if both members of the sample pair had evolved the same amounts of O_2, then the thickness of the product coatings would be similar, and the diffusional resistances to reactants would also be similar. Since the bulk diffusivity of H_2O and CO_2 reactants would be equivalent during the 1-atm portion of test No. KS-16 and during test No. KS-14, the rates of O_2 evolution and CO_2 absorption would therefore also be similar.

In the case of the $KO_2/Ca(O_2)_2$ mixture sample (test No. KS/CaS-5), it is apparent that there was complete recovery of the reactivity of the sample when the pressure was lowered from 10 atm to 1 atm, since the rates of O_2 evolution and CO_2 absorption at 1 atm are very close in magnitude to those of the sample reacted in test No. KS/CaS-3 at the same extent of reaction (table 14). It can be concluded, based on the similarity in rates of O_2 release and CO_2 absorption between the two 1-atm tests of the superoxide mixture samples, that the lower bulk diffusivity of the CO_2 and H_2O reactants in the 10-atm helium was the <u>primary</u> factor in reducing the hyperbaric reaction performance of the superoxide samples tested here.

However, in the case of the KO_2 granule samples (test Nos. KS-14 and KS-16), the rates of O_2 evolution and CO_2 absorption of the samples at a similar extent of reaction were dramatically different. In fact, the maximum rate of O_2 evolution for the 1-atm portion of test No. KS-16 was nearly identical to the rate seen at the end of the 10-atm portion of the same test. This continuation of the rates between the 1-atm and 10-atm portions of the test indicated in the case of KO_2 samples that there was no recovery of reaction performance once the dense helium diffusion barrier was removed.

The fact that the KO_2 granule samples exhibited no recovery from the poor hyperbaric reactivity upon being retested at 1 atm could be explained by secondary effects of the lower hyperbaric bulk diffusivity of the reactants. If the reaction rates were lower as a result of the mass-transfer limitation imposed by the bulk diffusivity, then the temperature of the reacting sample surface would be lower than at 1 atm because less exothermic heat of reaction would be released. The heat of reaction would also be carried away more rapidly by the high-density, hyperbaric helium stream. The resulting lower sample surface temperature would favor the formation of a hydrated hydroxide/carbonate product coating which would continue to limit the diffusion of reactants into the unreacted core of the sample even when the pressure was reduced to 1 atm.

It is interesting to note that although the inlet pH_2O during the KO_2 granule tests was 24.8 mm Hg and resulted in excellent utilization when a sample was reacted at 1 atm, the same partial pressure of H_2O resulted in one-seventh the utilization when a KO_2 granule was reacted at 10 atm. Therefore, although the 24.8-mm-Hg pH_2O level was very favorable to good utilization at the lower pressure (presumably via lack of formation of hydrous hydroxide/carbonate coatings), the same partial pressure of H_2O at 10 atm produced a low-permeability coating. The behavior of the $KO_2/Ca(O_2)_2$ sample (test No. KS/CaS-5) under the same dual-pressure regime indicated that a low-permeability coating was not being formed on the surface of the $KO_2/Ca(O_2)_2$ pellet even though the inlet pH_2O of 47 mm Hg was nearly twice that used in testing the KO_2 granules (test Nos. KS-14 and KS-16).

SUMMARY OF RESULTS

Laboratory-fabricated pellets made from powder mixtures of 50% KO_2-50% $Ca(O_2)_2$ and 76% KO_2-24% $Ca(O_2)_2$ exhibited superior reaction performance in comparison with similarly fabricated KO_2 pellets when the specimens were reacted with humidified CO_2/helium at 1 atm. The reaction performance of the superoxide pellets was evaluated based on the observed rates of O_2 evolution and CO_2 absorption, the utilization of the available O_2 and the CO_2 absorption capacity, and the physical characteristics of the reacted pellets.

The $KO_2/Ca(O_2)_2$ pellets evolved 2 times more O_2 and over 3 times more CO_2 than the KO_2 pellets when they were reacted under similar conditions. Of the two $KO_2/Ca(O_2)_2$ formulations, the 76% KO_2-24% $Ca(O_2)_2$ mixture exhibited the best reaction performance based on rate and utilization data. Whereas the product coating of the KO_2 pellet consisted of an undesirable, soft, mushy, fused, hydrated-hydroxide/carbonate layer, the product coating of the $KO_2/Ca(O_2)_2$ pellets was hard and nonfused.

When pellets of KO_2 and $KO_2/Ca(O_2)_2$ mixtures, as well as commercial KO_2 tablets and granules were reacted with humidified carbon dioxide/helium at 10 atm, the rates of O_2 evolution and CO_2 absorption and the utilization efficiency of the superoxide samples was one-third to one-eighth of that exhibited by similar samples tested at 1 atm. It has been postulated that this drop in reactivity under hyperbaric conditions is caused principally by the decrease in the bulk diffusivity of the H_2O and CO_2 reactants in the high-pressure helium, since the reactivity of a 50% KO_2-50% $Ca(O_2)_2$ pellet was completely restored when the pressure was lowered from 10 atm to 1 atm while the other reaction conditions were held constant.

In the case of KO_2, the lower bulk diffusivity of the CO_2 and H_2O in the hyperbaric helium stream has secondary effects on the reactivity of the samples. Since the exothermic reactions of H_2O and CO_2 with KO_2 were mass transfer limited via the helium diffusion barrier, the core temperature of the samples was 7-12°C lower than in the corresponding 1-atm tests. In addition, the sample surfaces were cooled more effectively by the higher heat capacity of the hyperbaric helium. This lower sample temperature favors the formation of a low-permeability hydrated-hydroxide/carbonate product coating which further limits the diffusion of CO_2 and H_2O into the KO_2 core. This coating prevents recovery of the reactivity of the KO_2 sample when the pressure is lowered from 10 atm to 1 atm.

CONCLUDING REMARKS

The use of potassium superoxide in portable life-support systems has been hampered in the past by the formation of a fused, hydrated-hydroxide/carbonate coating on the superoxide granules. Once this layer is formed, it limits the diffusion of H_2O and CO_2 reactants to the unreacted core of KO_2 and results in poor utilization of the available O_2 and the CO_2-scrubbing capacity. In the high-temperature environment of the exothermically reacting superoxide bed, the hydrated-hydroxide/carbonate coating also results in intergranule fusion such that sections of the packed bed are unavailable for reaction with the exhaled gas flow. This blockage reduces the utilization of the superoxide bed and also increases the resistance to breathing experienced by the user. If recycling of the breathing apparatus is desired, the fusion of the superoxide bed also makes it difficult to remove the expended chemical from the breathing canister.

On the basis of the results reported here it can be concluded that mixtures of KO_2 and $Ca(O_2)_2$ containing 25-50% by weight of $Ca(O_2)_2$ could alleviate the deleterious coating problem encountered with commercial KO_2 without a significant sacrifice in the overall available O_2 and CO_2-scrubbing capacities. The product coating on the superoxide mixture pellets tested here was permeable to H_2O and CO_2 reactants even at high inlet H_2O/CO_2 ratios and was also hard and nonfusing. A side benefit of the nonfusing nature of the coating on the $KO_2/Ca(O_2)_2$ pellets is that the expended superoxide material could be easily removed from the breathing canister and so recycling of the breathing device would be possible.

However, the application of the $KO_2/Ca(O_2)_2$ mixtures tested here to hyperbaric life-support systems is complicated by the presence of a dense helium atmosphere which apparently limits the diffusion of CO_2 and H_2O reactants through the gas phase to the unreacted core of the superoxide pellets or granules. This hyperbaric effect is not unique to the superoxide mixtures but would apply to any absorption/reaction process carried out under hyperbaric conditions. This adverse effect could be somewhat alleviated in breathing canister design by increasing the residence time of the exhaled reactant gas in the packed bed either by increasing the bed length or by decreasing the space velocity through the bed (e.g., by increasing the gas-flow cross sectional area). Because of the nonfusing nature of the $KO_2/Ca(O_2)_2$ mixtures, the particle size of the superoxide granules in the breathing canister could also be reduced somewhat, which would decrease the size of the intergranule void space through which the reactant gases must diffuse.

RECOMMENDATIONS FOR FURTHER RESEARCH

1. The research reported here indicated that a significant drop in the reactivity of KO_2 and $KO_2/Ca(O_2)_2$ mixtures toward humidified CO_2 occurred when the pressure was raised from 1 to 10 atm. Additional study of the reaction of these superoxides at intermediate pressures could provide further elucidation of the exact mechanism of the observed decline in reactivity and would give an indication of the useful pressure range over which satisfactory reaction performance from the superoxides could be expected.

2. Mixtures of KO_2 and $Ca(O_2)_2$ in the form of cylindrical pellets exhibited vastly superior reaction performance to similarly fabricated pellets of KO_2 when the superoxides were reacted at 1 atm with CO_2 humidified to a pH_2O of 47 mm Hg.

However, no tests were conducted in which the $KO_2/Ca(O_2)_2$ mixture pellets were reacted with CO_2 humidified with lower partial pressures of H_2O. Additional tests of the superoxide mixtures are needed to determine if the superior reaction performance of these materials would be exhibited at low to medium pH_2O levels. Also it would be of interest to determine the lower pH_2O limit at which satisfactory performance from the mixtures could be expected.

3. $KO_2/Ca(O_2)_2$ pellets were tested at an initial sample temperature of -40°C. The reaction performance of the superoxide mixtures at lower and higher temperatures was not evaluated and this temperature data would be important if the pellets were to be developed further for use in portable diving apparatus at various water temperatures.

4. Single pellets of $KO_2/Ca(O_2)_2$ mixtures were reacted with humidified carbon dioxide/helium at hyperbaric pressures. It would be of interest to test small beds of $KO_2/Ca(O_2)_2$ mixture granules at hyperbaric pressures to determine if the bulk diffusivity effects causing the poor reaction performance seen with the mixture pellets tested here, could be moderated by the increased contact time and lower void volume offered by the bed structure.

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TABLE 1.- COMPOSITION AND PHYSICAL CHARACTERISTICS OF SUPEROXIDE PELLETS

Test I.D. no.	Material[a] tested	Composition,[b] % KO_2/% $Ca(O_2)_2$	O_2 available, cm^3 STP g^{-1}	9.5-mm-diam pellet characteristics				
				Height, mm	Area,[c] cm^2	Volume, cm^3	Weight, g	Density, g/cm^3
KS-1	KO_2	100/0	204.9	7.0	3.52	0.499	0.65411	1.311
KS-2	KO_2	100/0	204.9	6.5	3.37	0.454	0.65925	1.360
KS-3	KO_2	100/0	204.9	6.8	3.46	0.484	0.64507	1.331
KS-4	KO_2	100/0	204.9	6.8	3.46	0.484	0.64197	1.325
KS-5	KO_2	100/0	204.9	6.7	3.43	0.477	0.63610	1.332
KS-6	KO_2	100/0	204.9	6.9	3.49	0.492	0.63741	1.296
KS-7	KO_2	100/0	204.9	7.1	3.55	0.506	0.66487	1.314
KS-8	KO_2	100/0	204.9	6.8	3.46	0.484	0.63873	1.318
KS-9	KO_2	100/0	204.9	6.0	3.22	0.428	0.59775	1.398
KS/CaS-1	$KO_2/Ca(O_2)_2$	75.7/24.3	195.0	6.1	3.22	0.435	0.50456	1.161
KS/CaS-2	$KO_2/Ca(O_2)_2$	75.7/24.3	195.0	7.0	3.52	0.498	0.56680	1.136
KS/CaS-3	$KO_2/Ca(O_2)_2$	50.5/49.5	194.4	7.2	3.58	0.513	0.51738	1.008
KS/CaS-4	$KO_2/Ca(O_2)_2$	50.5/49.5	194.4	7.3	3.61	0.520	0.52820	1.015
KS/CaS-5	$KO_2/Ca(O_2)_2$	50.5/49.5	194.4	6.8	3.46	0.484	0.48360	0.998

[a] Origin and composition of superoxides used in test samples: Test Nos. KS-1 through KS-9, KO_2 = MSA granules, ground to a grain size of <0.38 mm; 86.5% KO_2, remainder KOH, K_2CO_3 and $KHCO_3$. Test Nos. KS/CaS-1 through KS/CaS-2, KO_2 = MSA granules, ground to a grain size of <0.38 mm; 85.2% KO_2, remainder KOH, K_2CO_3, $KHCO_3$; $Ca(O_2)_2$ (from disproportionation of CaO_2 $2H_2O_2$ powder), 55.3% $Ca(O_2)_2$, 14.4% CaO_2, 30.3% $Ca(OH)_2$. Test Nos. KS/CaS-3 through KS/CaS-5, KO_2 = same as in test Nos. KS-1 through KS-9; $Ca(O_2)_2$ (from disproportionation of CaO_2 $2H_2O_2$ powder), 47.9% $Ca(O_2)_2$, 21.1% CaO_2, 31.0% $Ca(OH)_2$.

[b] The composition of the KO_2 and $Ca(O_2)_2$ source materials used to make mixtures are given in footnote "a."

[c] Area = geometric surface area of the pellet before the start of the test.

TABLE 2.- COMPOSITION AND PHYSICAL CHARACTERISTICS OF POTASSIUM SUPEROXIDE GRANULES AND TABLETS

Test I.D. no.	Material[a] tested	Composition,[b] % KO_2	O_2 capacity, cm^3 STP g^{-1}	Granule[c] or tablet characteristic		
				Diameter, mm	Height, mm	Weight, g
KS-10	KO_2 tablet	76.1	180.0	9.0	4.6	0.24771
KS-11	KO_2 granule	90.7	215.1	9.5	5.9	0.23803
KS-12	KO_2 tablet	76.1	180.0	9.0	4.6	0.24784
KS-13	KO_2 tablet	76.1	180.0	9.0	4.6	0.25397
KS-14	KO_2 granule	90.7	215.1	9.5	5.3	0.24412
KS-15	KO_2 granule	90.7	215.1	9.5	9.0	0.38250
KS-16	KO_2 granule	90.7	215.1	9.5	5.3	0.27408

[a] Tablets were taken from a Drager OXY SR 60B portable breathing device; granules were taken from an MSA 60-min portable breathing device (Part No. 4644213).

[b] The remainder of the sample is a mixture of KOH, K_2CO_3, and $KHCO_3$, except for the tablets, which also contained traces of a transition metal catalyst.

[c] Only the largest dimensions of the granules are listed under diameter and height because the granules were of irregular shape.

TABLE 3.- FLOW-SYSTEM REACTION CONDITIONS FOR TESTING 9.5-mm SUPEROXIDE PELLETS

Test I.D. no.	Material tested	Absolute pressure, atm	Inlet pCO_2, mm Hg	Inlet H_2O		Flow rate at pressure, $cm^3\ min^{-1}$	Inlet H_2O/CO_2 ratio
				Dew point, °C	pH_2O, mm Hg		
KS-1[a]	KO_2	1.09	41.4	37.0	47.1	308	1.14
KS-2	KO_2	1.09	41.5	36.9	46.9	315	1.13
KS-3	KO_2	9.99	38.3	37.1	47.3	323	1.24
KS-4	KO_2	9.99	38.4	36.8	46.6	323	1.21
KS-5	KO_2	1.09	41.4	24.9	23.6	314	0.57
KS-6	KO_2	1.09	41.4	20.1	17.7	314	0.42
KS-7	KO_2	9.99	38.4	20.2	17.7	323	0.46
KS-8[b]	KO_2	10.00	38.4	20.2	17.8	343	0.46
KS-9	KO_2	1.09	41.6	-78.0	0	315	0
KS/CaS-1	$KO_2/Ca(O_2)_2$	1.09	41.4	36.9	46.9	314	1.13
KS/CaS-2	$KO_2/Ca(O_2)_2$	10.00	38.4	36.8	46.7	323	1.22
KS/CaS-3	$KO_2/Ca(O_2)_2$	1.10	41.8	37.0	47.1	312	1.13
KS/CaS-4	$KO_2/Ca(O_2)_2$	10.00	38.3	37.0	47.1	323	1.23
KS/CaS-5[c]	$KO_2/Ca(O_2)_2$	10.01	38.1	36.9	46.9	323	1.23
		1.09	41.9	36.9	46.9	309	1.12

[a] Diluent gas in this test was nitrogen.
[b] Reactor temperature was 60.3°C for this test only.
[c] Sample was reacted at ~10 atm for 1.5 ksec and then at ~1 atm for 1.5 ksec.

TABLE 4.- FLOW-SYSTEM REACTION CONDITIONS FOR TESTING POTASSIUM SUPEROXIDE GRANULES AND TABLETS

Test I.D. no.	Material tested	Absolute pressure, atm	Inlet pCO_2, mm Hg	Inlet H_2O		Flow rate at pressure, $cm^3 min^{-1}$	Inlet H_2O/CO_2 ratio
				Dew point, °C	pH_2O, mm Hg		
KS-10	KO_2 tablet	1.09	41.5	37.1	47.4	313	1.14
KS-11	KO_2 granule	1.09	41.6	37.3	47.8	313	1.15
KS-12	KO_2 tablet	1.09	41.6	24.8	23.5	313	0.56
KS-13	KO_2 tablet	10.00	38.0	24.9	23.6	323	0.62
KS-14	KO_2 granule	1.09	41.6	24.7	23.4	313	0.56
KS-15	KO_2 granule	10.00	38.8	24.8	23.5	323	0.61
KS-16[a]	KO_2 granule	10.00	38.0	24.9	23.7	323	0.62
		1.09	41.4	25.0	23.7	313	0.57

[a] Sample was reacted at ~10 atm for 1.5 ksec, and then at ~1 atm for 1.5 ksec.

TABLE 5.- RATES OF OXYGEN EVOLUTION AND CARBON DIOXIDE ABSORPTION DURING REACTION OF SUPEROXIDE PELLETS WITH HUMIDIFIED CARBON DIOXIDE

Test I.D.[a] no.	Material tested	Maximum rates				Average rates			
		O_2 evolution		CO_2 absorption		O_2 evolution		CO_2 absorption	
		μmol s^{-1}	μmol s^{-1} cm^{-2}	μmol s^{-1}	μmol s^{-1} cm^{-2}	μmol s^{-1}	μmol s^{-1} g^{-1}	μmol s^{-1}	μmol s^{-1} g^{-1}
KS-1	KO_2	4.36	1.24	6.52	1.85	1.19	1.82	0.96	1.47
KS-2	KO_2	5.12	1.52	8.41	2.50	1.63	2.47	0.83	1.26
(KS-3)	KO_2	1.83	0.53	2.97	0.86	1.65	2.55	0.53	0.83
(KS-4)	KO_2	1.99	0.58	2.69	0.78	1.66	2.59	0.69	1.08
KS-5	KO_2	3.96	1.15	8.57	2.50	1.81	2.85	1.53	2.41
KS-6	KO_2	4.04	1.16	8.61	2.47	2.31	3.63	2.02	3.17
(KS-7)	KO_2	1.21	0.34	2.62	0.74	0.57	0.86	0.47	0.70
(KS-8)	KO_2	1.34	0.39	3.70	1.07	0.82	1.28	1.02	1.59
KS-9	KO_2	1.69	0.52	7.26	2.25	0.55	0.92	0.80	1.34
KS/CaS-1	$KO_2/Ca(O_2)_2$	10.80	3.35	8.55	2.65	2.53	5.02	2.32	4.61
(KS/CaS-2)	$KO_2/Ca(O_2)_2$	2.51	0.71	2.64	0.75	1.45	2.55	0.46	0.82
KS/CaS-3	$KO_2/Ca(O_2)_2$	6.01	1.68	7.76	2.17	2.45	4.74	2.29	4.43
(KS/CaS-4)	$KO_2/Ca(O_2)_2$	2.02	0.56	2.67	0.74	1.15	2.21	0.89	1.72
(KS/CaS-5)[b]	$KO_2/Ca(O_2)_2$	2.06	0.60	2.35	0.68	1.16	2.40	0.74	1.54

[a] Test numbers in parentheses indicate that testing was carried out at 10 atm.

[b] Rate data are for 10 atm portion of test only.

TABLE 6.- RATES OF OXYGEN EVOLUTION AND CARBON DIOXIDE ABSORPTION DURING REACTION OF POTASSIUM SUPEROXIDE GRANULES AND TABLETS WITH HUMIDIFIED CARBON DIOXIDE

Test I.D.[a] no.	Material tested	Maximum rates		Average rates			
		O_2 evolution	CO_2 absorption	O_2 evolution		CO_2 absorption	
		μmol s^{-1}	μmol s^{-1}	μmol s^{-1}	μmol s^{-1} g^{-1}	μmol s^{-1}	μmol s^{-1} g^{-1}
KS-10	KO_2 tablet	9.74	6.97	1.32	5.33	0.70	2.81
KS-11	KO_2 granule	4.78	6.43	0.87	3.64	0.79	3.32
KS-12	KO_2 tablet	7.35	6.97	1.35	5.46	1.04	4.19
(KS-13)	KO_2 tablet	1.56	1.55	0.35	1.40	0.18	0.71
KS-14	KO_2 granule	4.81	6.37	1.39	5.69	1.69	6.92
(KS-15)	KO_2 granule	ND	ND	0.44	1.14	0.34	0.90
(KS-16)[b]	KO_2 granule	1.06	1.88	0.39	1.41	0.35	1.26

[a] Test numbers in parentheses indicate that testing was carried out at 10 atm.
[b] Rate data are for 10 atm portion of test only.

TABLE 7.- AMOUNTS OF OXYGEN EVOLVED AND CARBON DIOXIDE ABSORBED DURING THE REACTION OF SUPEROXIDE PELLETS WITH HUMIDIFIED CARBON DIOXIDE

Test I.D.[b] no.	Material tested	Amount of gas evolved or absorbed[a]		
		O_2 evolved		CO_2 absorbed
		cm^3 STP g^{-1}	% Available	cm^3 STP g^{-1}
KS-1	KO_2	61.0	29.8	49.3
KS-2	KO_2	83.0	40.5	42.4
(KS-3)	KO_2	85.8	41.9	27.8
(KS-4)	KO_2	87.1	42.5	36.3
KS-5	KO_2	95.8	46.7	81.1
KS-6	KO_2	122.0	59.5	106.5
(KS-7)	KO_2	28.8	14.0	23.6
(KS-8)	KO_2	43.2	21.1	53.4
KS-9	KO_2	30.8	15.1	45.1
KS/CaS-1	$KO_2/Ca(O_2)_2$	168.6	86.5	154.8
(KS/CaS-2)	$KO_2/Ca(O_2)_2$	85.8	44.0	27.5
KS/CaS-3	$KO_2/Ca(O_2)_2$	159.3	82.0	148.9
(KS/CaS-4)	$KO_2/Ca(O_2)_2$	74.2	38.2	57.6
(KS/CaS-5)[c]	$KO_2/Ca(O_2)_2$	80.8	41.5	51.8

[a] During 1.5 ksec of reaction.

[b] Test numbers in parentheses indicate that testing was carried out at 10 atm.

[c] Amounts are for 10-atm portion of test only.

TABLE 8.- AMOUNTS OF OXYGEN EVOLVED AND CARBON DIOXIDE ABSORBED DURING THE REACTION OF POTASSIUM SUPEROXIDE GRANULES AND TABLETS WITH HUMIDIFIED CARBON DIOXIDE

Test I.D.[b] no.	Material tested	Amount of gas evolved or absorbed[a]		
		O_2 evolved		CO_2 absorbed
		cm^3 STP g^{-1}	% available	cm^3 STP g^{-1}
KS-10	KO_2 tablet	179.2	99.5	94.4
KS-11	KO_2 granule	122.3	56.8	111.5
KS-12	KO_2 tablet	183.6	102.0	140.9
(KS-13)	KO_2 tablet	47.2	26.2	23.8
KS-14	KO_2 granule	191.3	88.9	232.5
(KS-15)	KO_2 granule	38.3	17.8	30.3
(KS-16)[c]	KO_2 granule	47.4	22.0	42.4

[a] During 1.5 ksec of reaction.

[b] Test numbers in parentheses indicate that testing was carried out at 10 atm.

[c] Amounts are for 10 atm portion of test only.

TABLE 9.- PHYSICAL CHARACTERISTICS OF 9.5 mm SUPEROXIDE PELLETS AFTER REACTION WITH HUMIDIFIED CARBON DIOXIDE

Test I.D.[a] no.	Material tested	Pellet shape[b]	Product-coating consistency[c]	Coating thickness, t, mm
KS-1	KO_2	Face erosion	Soft faces, hard equator	$0.5 < t < 1.5$
KS-2	KO_2	Swollen	Soft, mushy, w/bubbles	$0.5 < t < 1.5$
(KS-3)	KO_2	Face erosion	Soft, mushy, w/bubbles	$0.5 < t < 1.5$
(KS-4)	KO_2	Face erosion	Soft, mushy, w/bubbles	$0.5 < t < 1.5$
KS-5	KO_2	N.C.	Hard	$0.5 < t < 1.5$
KS-6	KO_2	N.C.	Hard	$0.5 < t < 1.5$
(KS-7)	KO_2	N.C.	Hard	$t < 0.5$
(KS-8)	KO_2	N.C.	Hard	$t < 0.5$
KS-9	KO_2	N.O.	N.O.	N.O.
KS/CaS-1	$KO_2/Ca(O_2)_2$	N.C.	Hard	$t > 1.5$
(KS/CaS-2)	$KO_2/Ca(O_2)_2$	Slight distortion	Hard	$0.5 < t < 1.5$
KS/CaS-3	$KO_2/Ca(O_2)_2$	N.C.	Hard	$t > 1.5$
(KS/CaS-4)	$KO_2/Ca(O_2)_2$	N.C.	Hard	$0.5 < t < 1.5$
(KS/CaS-5)	$KO_2/Ca(O_2)_2$	N.C.	Hard	$t > 1.5$[d]

[a] Test numbers in parentheses indicate that testing was carried out at 10 atm.

[b] N.C. = no change from pretest shape, N.O. = not observed.

[c] Hardness of the coating was evaluated by probing with a razor-blade knife tip.

[d] Thickness was measured after 3.0 ksec of reaction (1.5 ksec at ~10 atm and 1.5 ksec at ~1 atm).

TABLE 10.- PHYSICAL CHARACTERISTICS OF POTASSIUM SUPEROXIDE TABLETS AND GRANULES AFTER REACTION WITH HUMIDIFIED CARBON DIOXIDE

Test I.D.[a] no.	Material tested	Sample shape[b]	Product-coating consistency[c]	Coating thickness, t, mm
KS-10	KO_2 tablet	Swollen	Hard outside, soft inside	$t > 1.5$
KS-11	KO_2 granule	N.C.	Semi-hard, crusty	$t < 0.5$
KS-12	KO_2 tablet	N.C.	Hard	$t > 1.5$
(KS-13)	KO_2 tablet	Slight distortion	Semi-hard	$t < 0.5$
KS-14	KO_2 granule	N.C.	Hard	$t > 1.5$
(KS-15)	KO_2 granule	N.C.	Hard	$t < 0.5$
(KS-16)	KO_2 granule	N.C.	Semi-hard	$t < 0.5$[d]

[a] Test numbers in parentheses indicate that testing was carried out at 10 atm.

[b] N.C. = no change from pretest shape.

[c] Hardness of the coating was evaluated by probing with a razor-blade knife tip.

[d] Thickness was measured after 3.0 ksec of reaction (1.5 ksec at ~10 atm and 1.5 ksec at ~1 atm).

TABLE 11.- MAXIMUM SAMPLE TEMPERATURES OBSERVED DURING TESTING OF 9.5-mm-diam SUPEROXIDE PELLETS

Test I.D.[a] no.	Material tested	Maximum sample[b] temperature, °C	T(sample)-T(reactor),[c] °C
KS-1	KO_2	57.7	18.2
KS-2	KO_2	48.3	8.7
(KS-3)	KO_2	40.7	1.5
(KS-4)	KO_2	41.1	1.7
KS-5	KO_2	48.3	8.7
KS-6	KO_2	47.0	7.6
(KS-7)	KO_2	39.9	0.5
(KS-8)	KO_2	60.2	-0.1
KS-9	KO_2	43.0	3.5
KS/CaS-1	$KO_2/Ca(O_2)_2$	56.6	17.1
(KS/CaS-2)	$KO_2/Ca(O_2)_2$	40.5	1.0
KS/CaS-3	$KO_2/Ca(O_2)_2$	56.1	16.8
(KS/CaS-4)	$KO_2/Ca(O_2)_2$	40.4	0.9
(KS/CaS-5)[d]	$KO_2/Ca(O_2)_2$	40.1 (10 atm)	0.6
		45.0 (1 atm)	5.6

[a] Test numbers in parentheses indicate that testing was carried out at 10 atm.

[b] Temperature measured at the approximate center of the sample.

[c] Reactor temperature ranges from 39.2 to 39.6°C except in Test no. KS-8, in which the reactor temperature was 60.3°C.

[d] Sample reacted at 10 atm for 1.5 ksec, then at 1 atm for 1.5 ksec.

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TABLE 12.- MAXIMUM SAMPLE TEMPERATURES OBSERVED DURING TESTING OF COMMERCIAL POTASSIUM SUPEROXIDE GRANULES AND TABLETS

Test I.D.[a] no.	Material tested	Maximum sample[b] temperature, °C	T(sample)-T(reactor),[c] °C
KS-10	KO_2 tablet	51.1	11.6
KS-11	KO_2 granule	45.1	5.7
KS-12	KO_2 tablet	51.1	11.7
(KS-13)	KO_2 tablet	39.6	0.1
KS-14	KO_2 granule	49.5	10.0
(KS-15)	KO_2 granule	39.4	-0.3
(KS-16)[d]	KO_2 granule	39.4 (10 atm)	-0.1
		40.1 (1 atm)	0.6

[a] Test numbers in parentheses indicate that testing was carried out at 10 atm.

[b] Temperature measured at the approximate center of mass of the sample.

[c] Reactor temperature ranged from 39.4-39.5°C.

[d] Sample reacted at 10 atm for 1.5 ksec, then at 1 atm for 1.5 ksec.

TABLE 13.- BULK DIFFUSIVITIES OF CARBON DIOXIDE AND WATER VAPOR IN HELIUM AT 1 atm

Gas temperature, °C (K)	Diffusivity,[a] $cm^2\ s^{-1}$				Ratio D_{He-H_2O}/D_{He-CO_2}
	$He-H_2O$		$He-CO_2$		
	1 atm	10 atm	1 atm	10 atm	
10 (283)	0.787	0.0787	0.530	0.0530	1.49
20 (293)	0.836	0.0836	0.569	0.0569	1.47
30 (303)	0.884	0.0884	0.608	0.0608	1.45
40 (313)	0.932	0.0932	0.648	0.0648	1.44
50 (323)	0.980	0.0980	0.687	0.0687	1.43
60 (333)	1.029	0.1029	0.726	0.0726	1.42
70 (343)	1.077	0.1077	0.765	0.0765	1.41
80 (353)	1.125	0.1125	0.804	0.0804	1.40
90 (363)	1.174	0.1174	0.844	0.0844	1.39
100 (373)	1.222	0.1222	0.883	0.0883	1.38
110 (383)	1.270	0.1270	0.922	0.0922	1.38
120 (393)	1.318	0.1318	0.961	0.0961	1.37

[a] Calculated from linear regressions of the experimental data listed in reference 30.

TABLE 14.- RECOVERY OF REACTIVITY FOR SUPEROXIDE SAMPLES RETESTED AT 1 atm AFTER REACTION AT 10 atm

	Test I.D. no.	
	KS-16	KS/CaS-5
O_2 evolved, cm^3 STP g^{-1}		
10-atm test phase	47.4	80.8
Interphase equilibration period	8.0	8.5
Subtotal (prior to 1-atm test phase)	55.4	89.3
1-atm test phase	31.6	54.0
Total	87.0	143.3
Expected (based on O_2 evolved by a similar sample at 1 atm)	191.3[a]	159.3[b]
Rate O_2 evolution, μmol s^{-1}		
10-atm test phase		
Maximum	1.06	2.06
At 1.5 ksec	0.28	0.70
1-atm test phase		
Maximum	0.31	2.61
At 1.5 ksec	0.22	0.15
Expected maximum[c]	3.42[a]	2.75[b]
CO_2 absorbed, cm^3 STP g^{-1}		
10-atm test phase	42.4	51.8
Interphase equilibration period	0	0
Subtotal (prior to 1-atm test phase)	42.4	51.8
1-atm test phase	74.0	141.2
Total	116.4	193.0
Expected (based on CO_2 evolved by a similar sample at 1 atm)	232.5[a]	148.9[b]
Rate CO_2 absorption, μmol s^{-1}		
10-atm test phase		
Maximum	1.88	2.35
At 1.5 ksec	0.20	0.40
1-atm test phase		
Maximum	0.80	2.50
At 1.5 ksec	0.20	1.40
Expected maximum[c]	3.60[a]	2.40[b]

[a] Test no. KS-14.
[b] Test no. KS/CaS-3.
[c] Rate of a similar sample at the same extent of utilization. The extent of utilization determined by O_2 evolved prior to a 1-atm test phase.

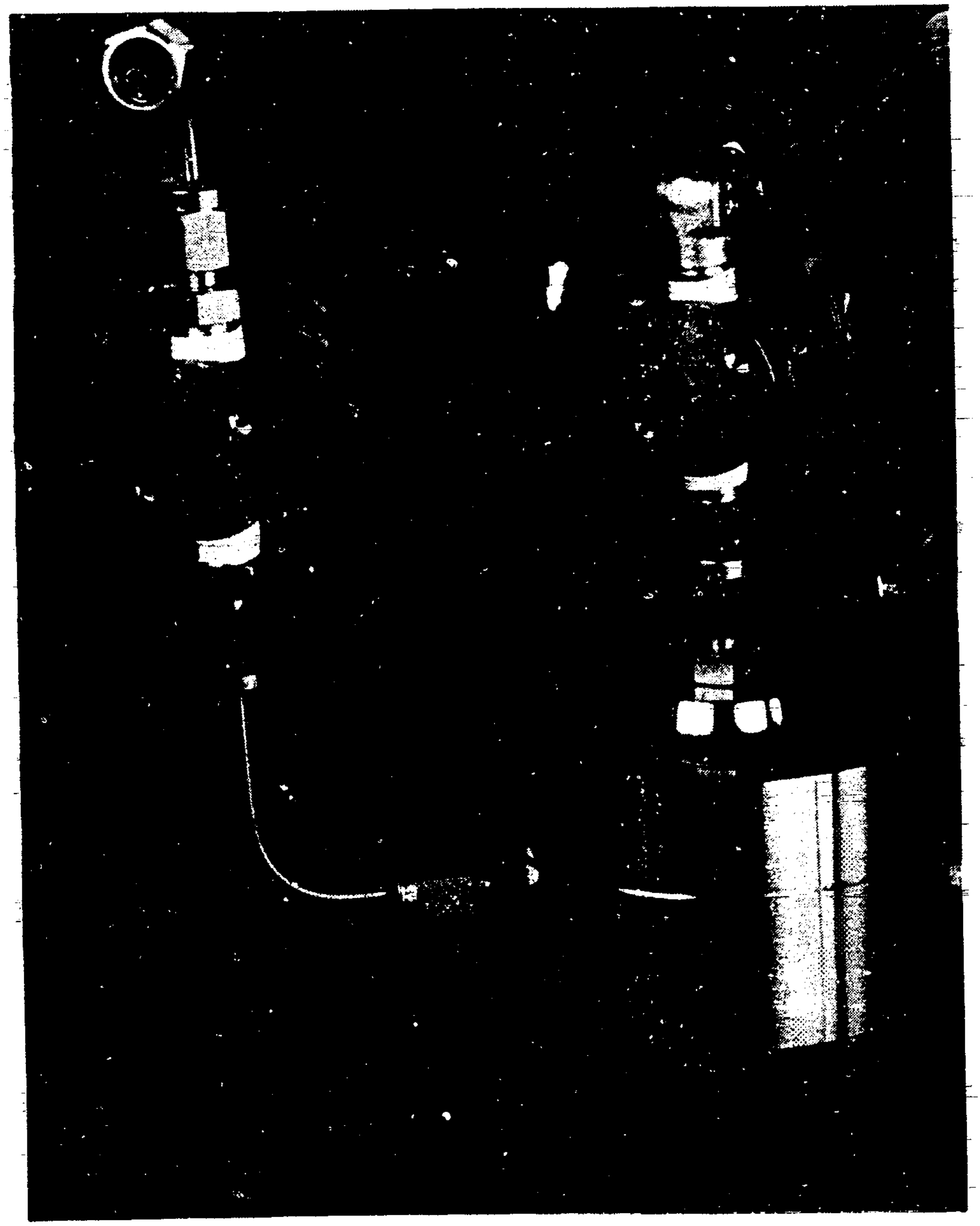


Figure 1.- Assembled single-pellet hyperbaric reactor used for testing superoxide samples.

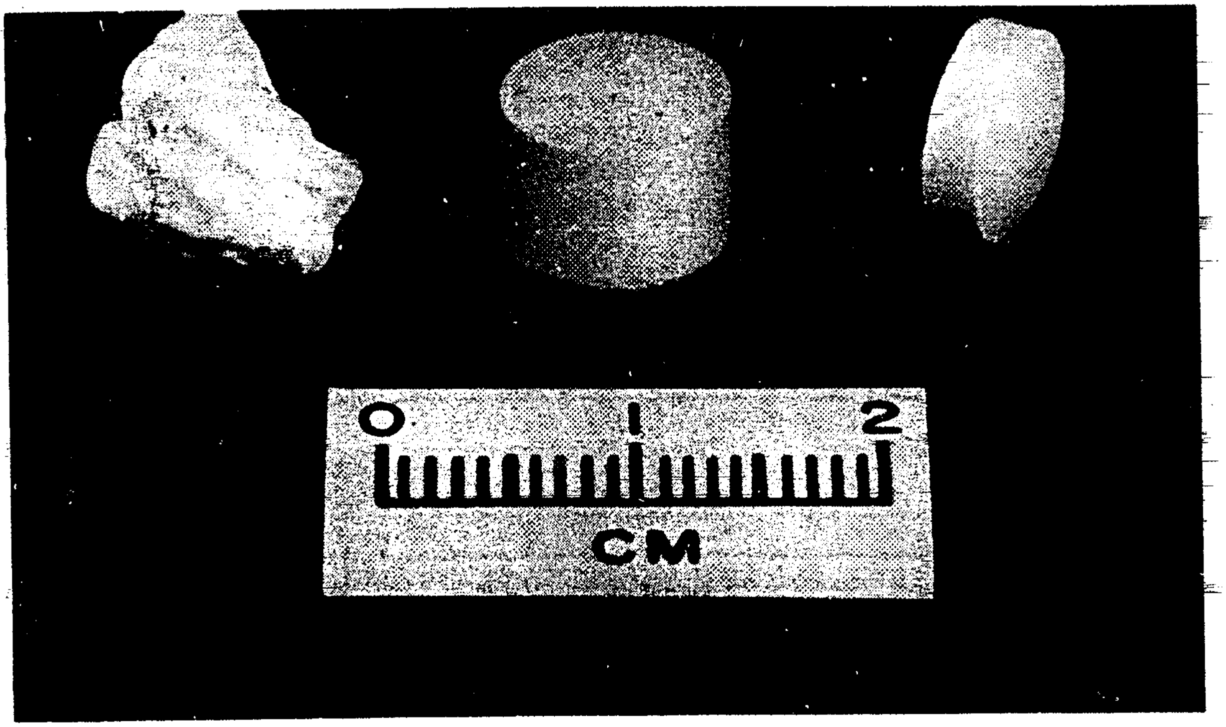


Figure 2.- Superoxide test-sample types: laboratory-fabricated pellet (center), commercial KO_2 granule (left), and tablet (right).

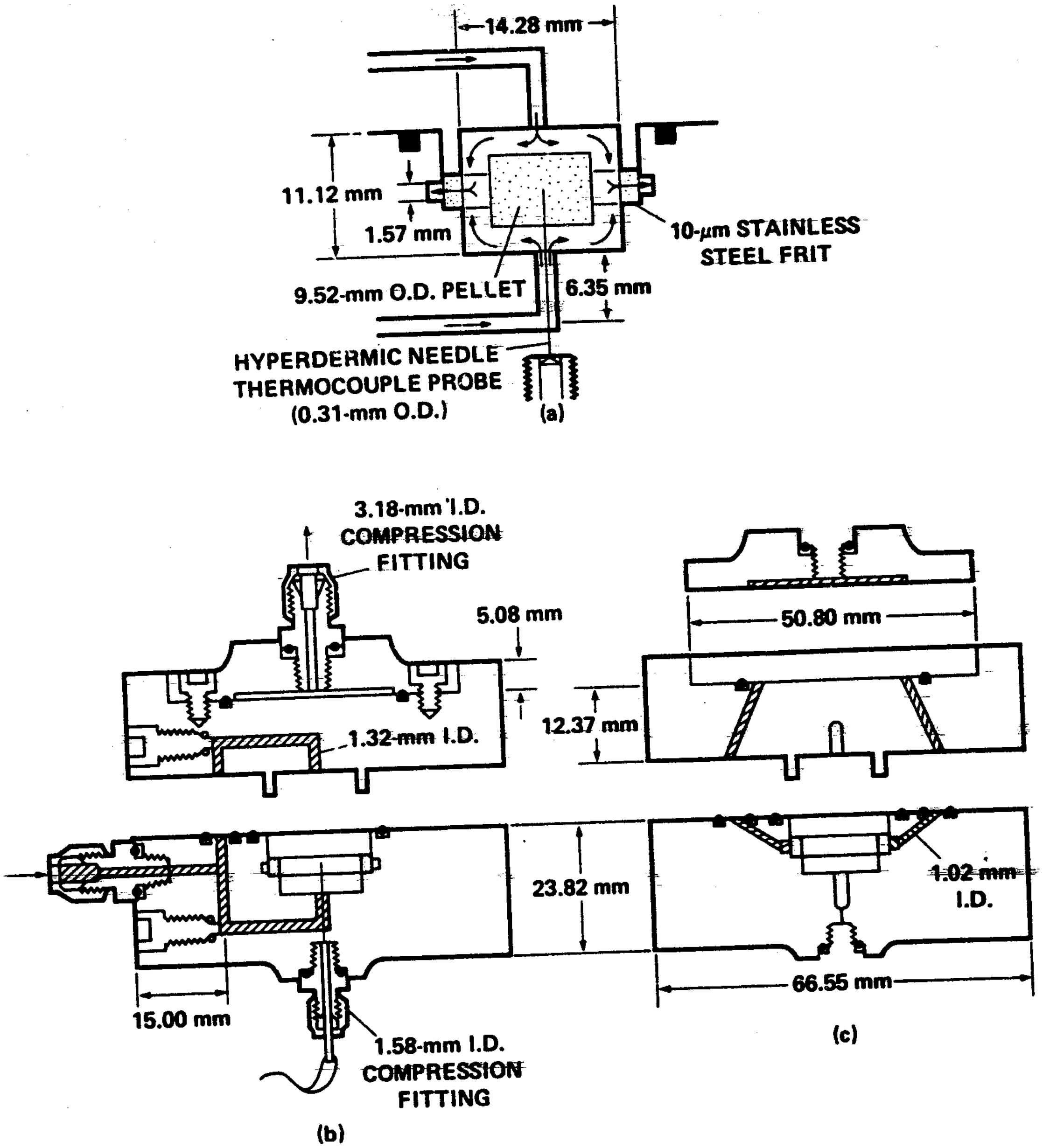


Figure 3.- Cutaway drawings of hyperbaric reactor interior. (a) Close up of superoxide pellet and gas-flow path. (b) Upper and lower halves of reactor showing inlet gas-flow path. (c) Upper and lower reactor halves showing outlet gas-flow path.

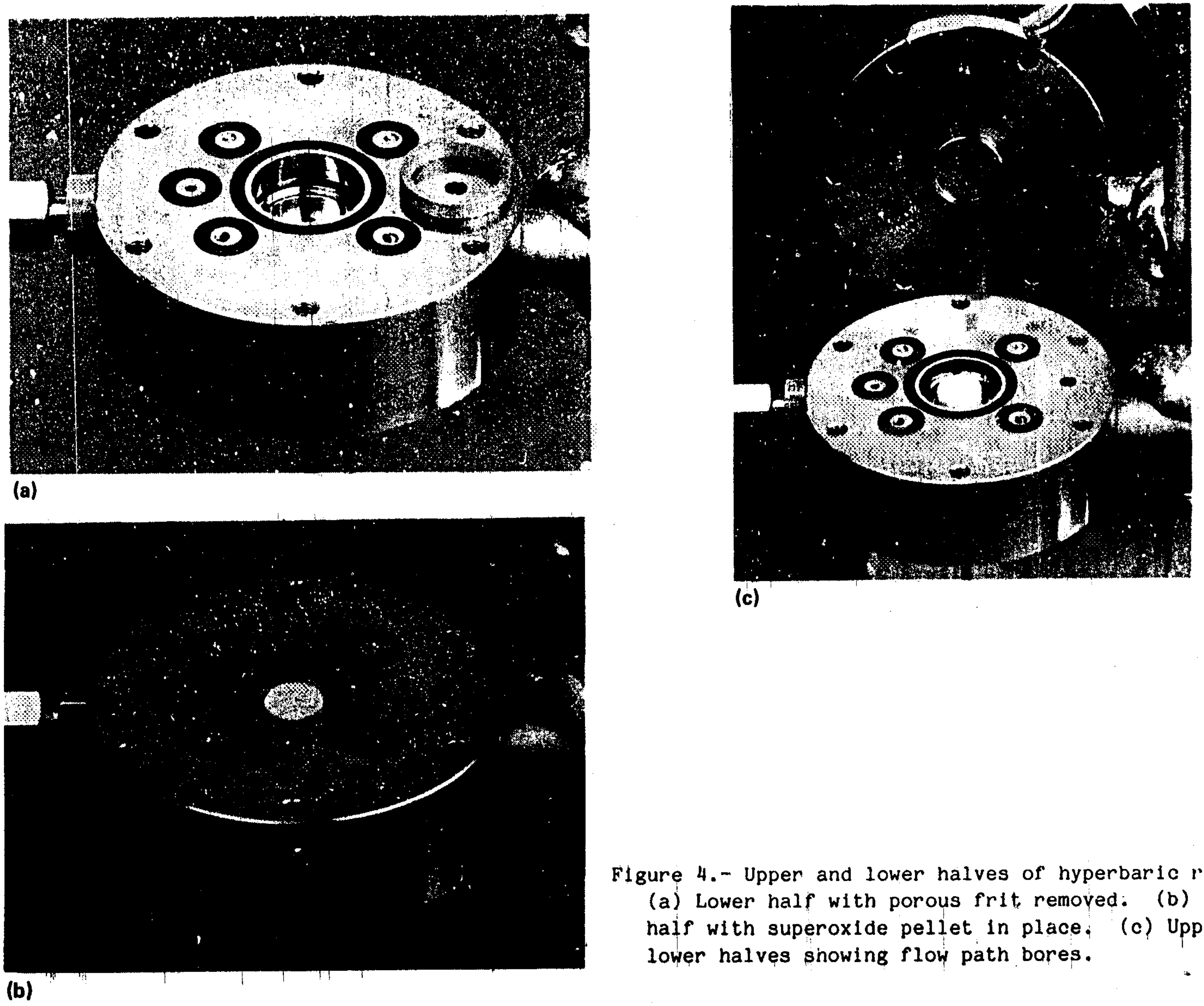
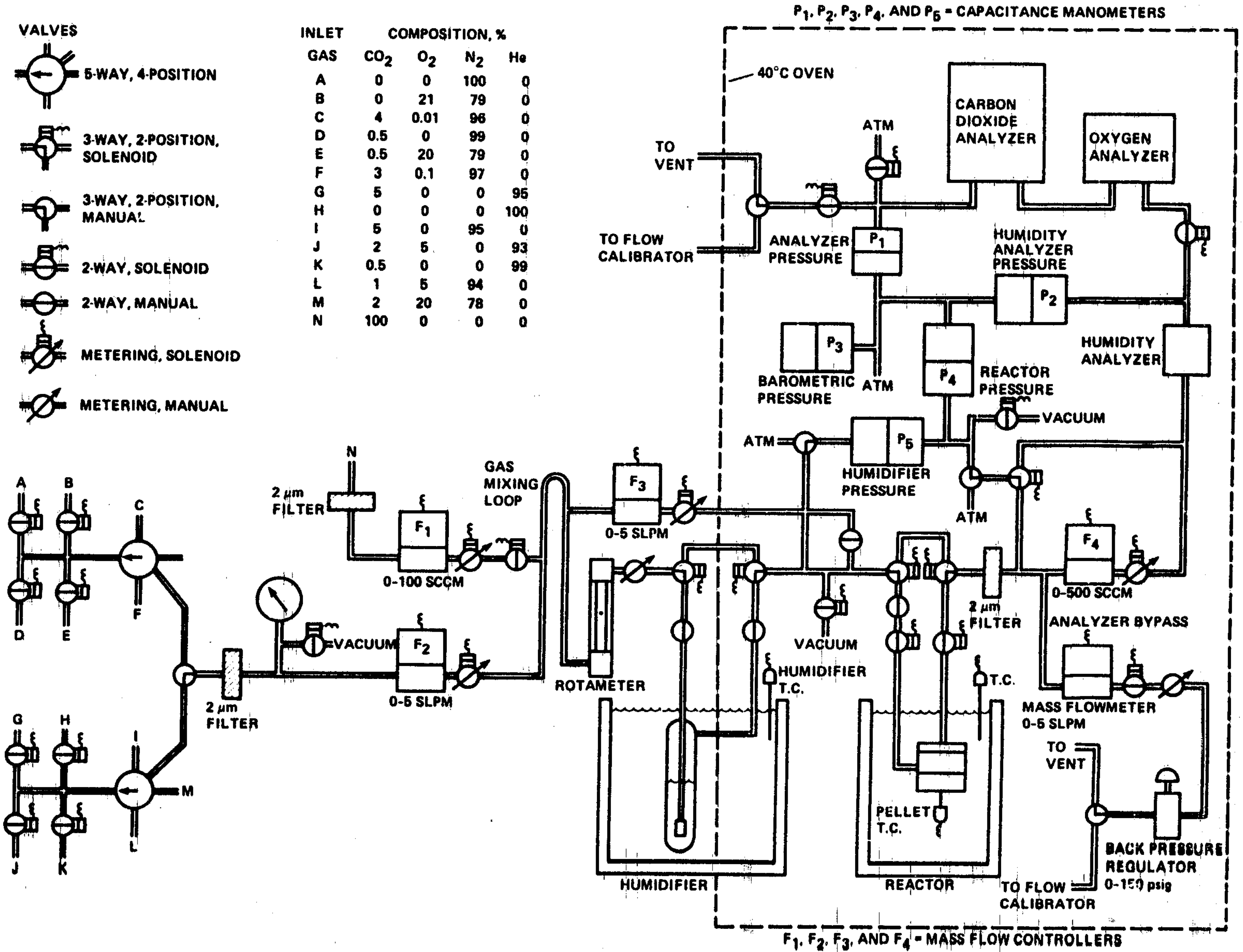


Figure 4.- Upper and lower halves of hyperbaric reactor. (a) Lower half with porous frit removed. (b) Lower half with superoxide pellet in place. (c) Upper and lower halves showing flow path bores.



INLET GAS	COMPOSITION, % CO_2	O_2	N_2	He
A	0	0	100	0
B	0	21	79	0
C	4	0.01	96	0
D	0.5	0	99	0
E	0.5	20	79	0
F	3	0.1	97	0
G	5	0	0	95
H	0	0	0	100
I	5	0	95	0
J	2	5	0	93
K	0.5	0	0	99
L	1	5	94	0
M	2	20	78	0
N	100	0	0	0

Figure 5.- Hyperbaric, single-pass, flow-system test facility.

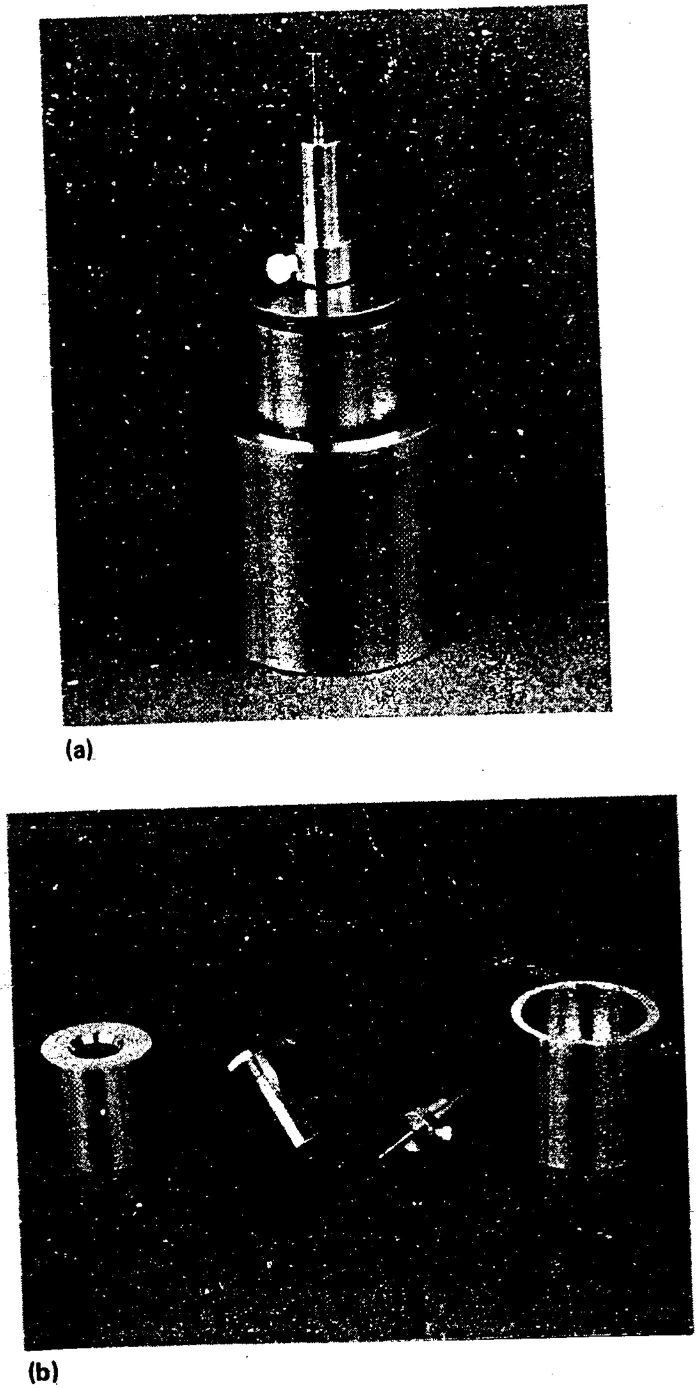


Figure 6.- Superoxide sample hand drill. (a) Assembled drill. (b) Diassembled drill showing (from left to right) 9.52-mm-i.d. pellet die, drill guide, drill shaft, and base.

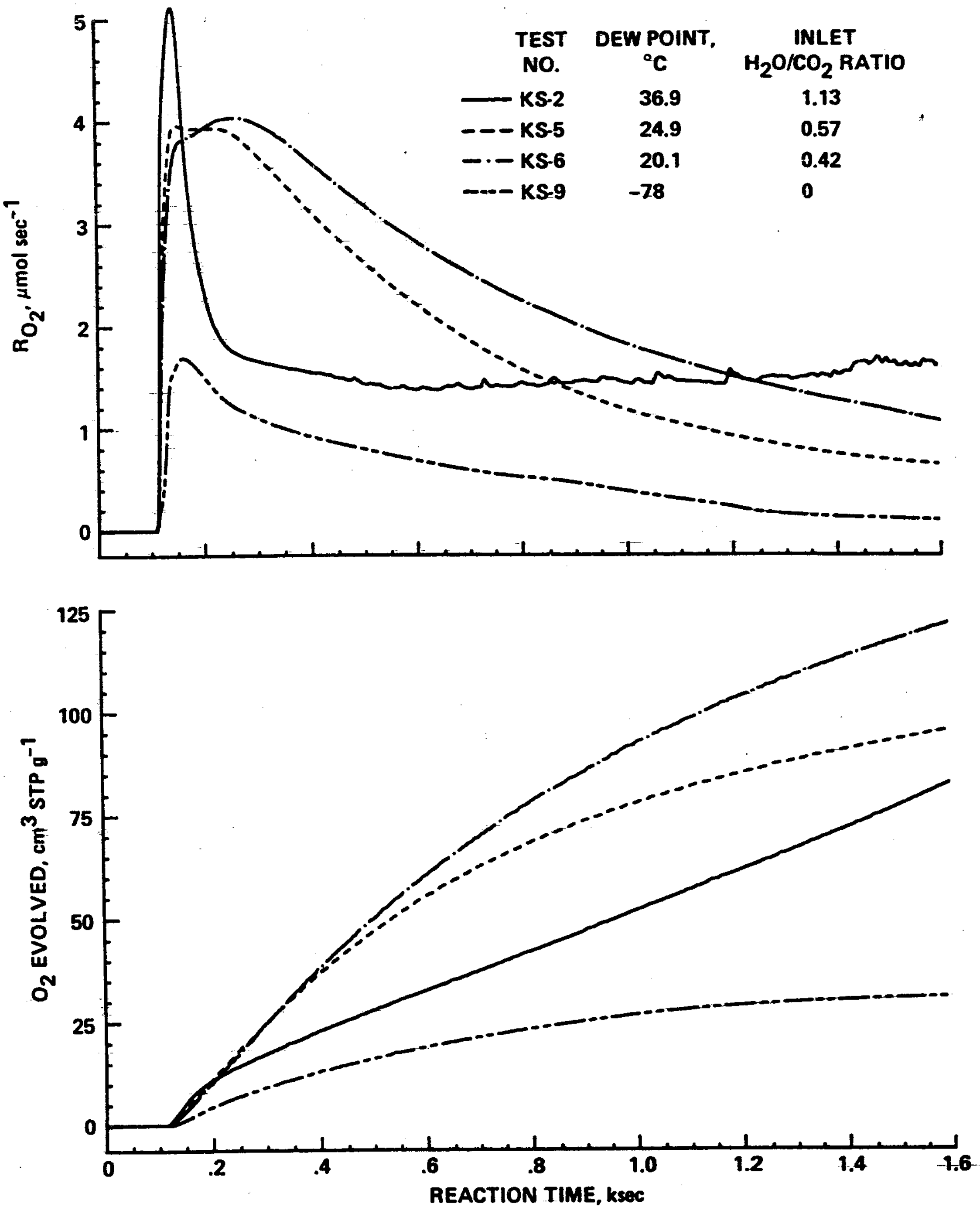


Figure 7.- Reaction of KO_2 pellets with humidified carbon dioxide/helium. Rates of O_2 evolution and amounts of O_2 evolved as a function of reaction time at 1-atm total pressure.

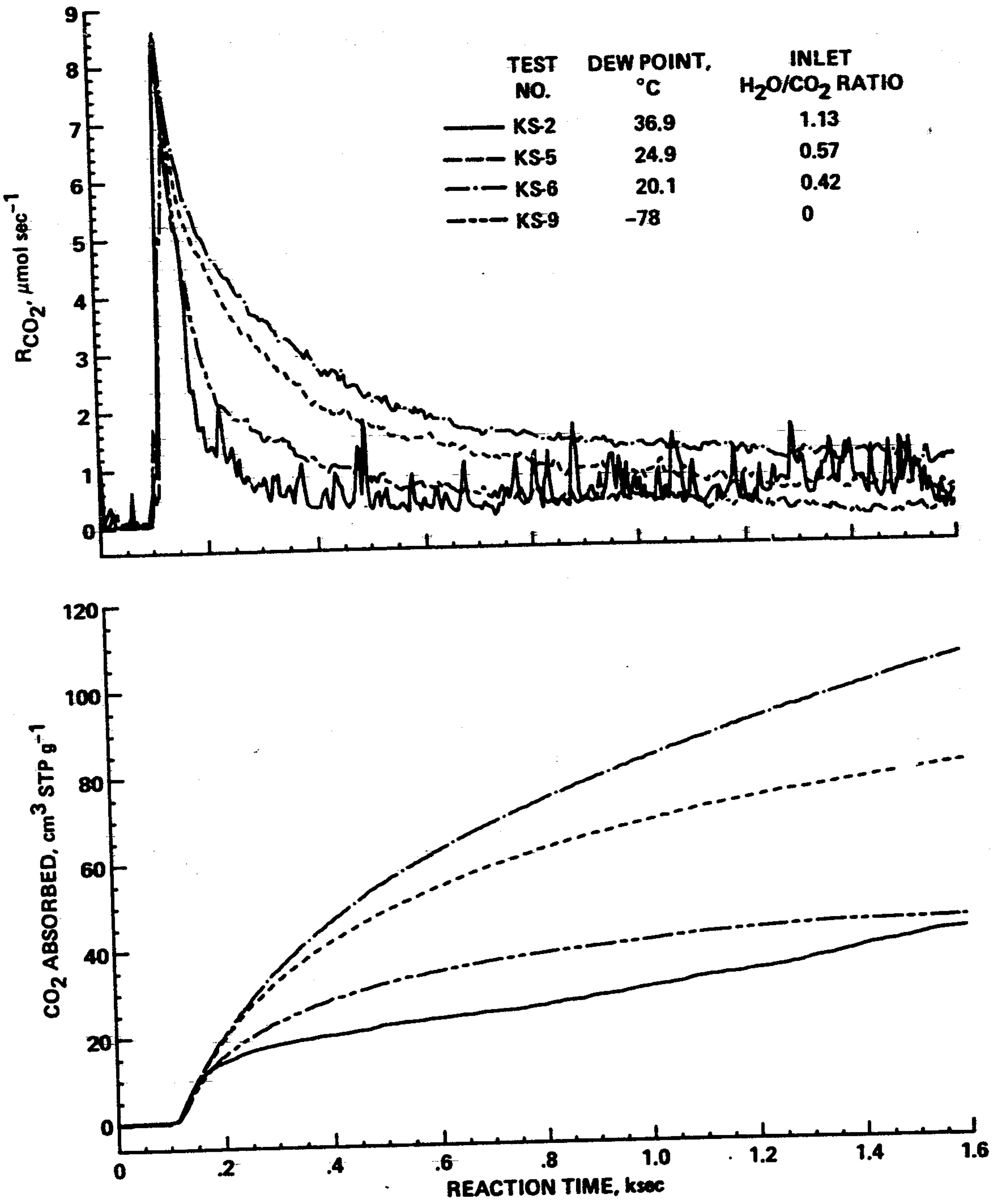


Figure 8.- Reaction of KO_2 pellets with humidified carbon dioxide/helium. Rates of CO_2 absorption and amounts of CO_2 absorbed as a function of reaction time at 1-atm total pressure.

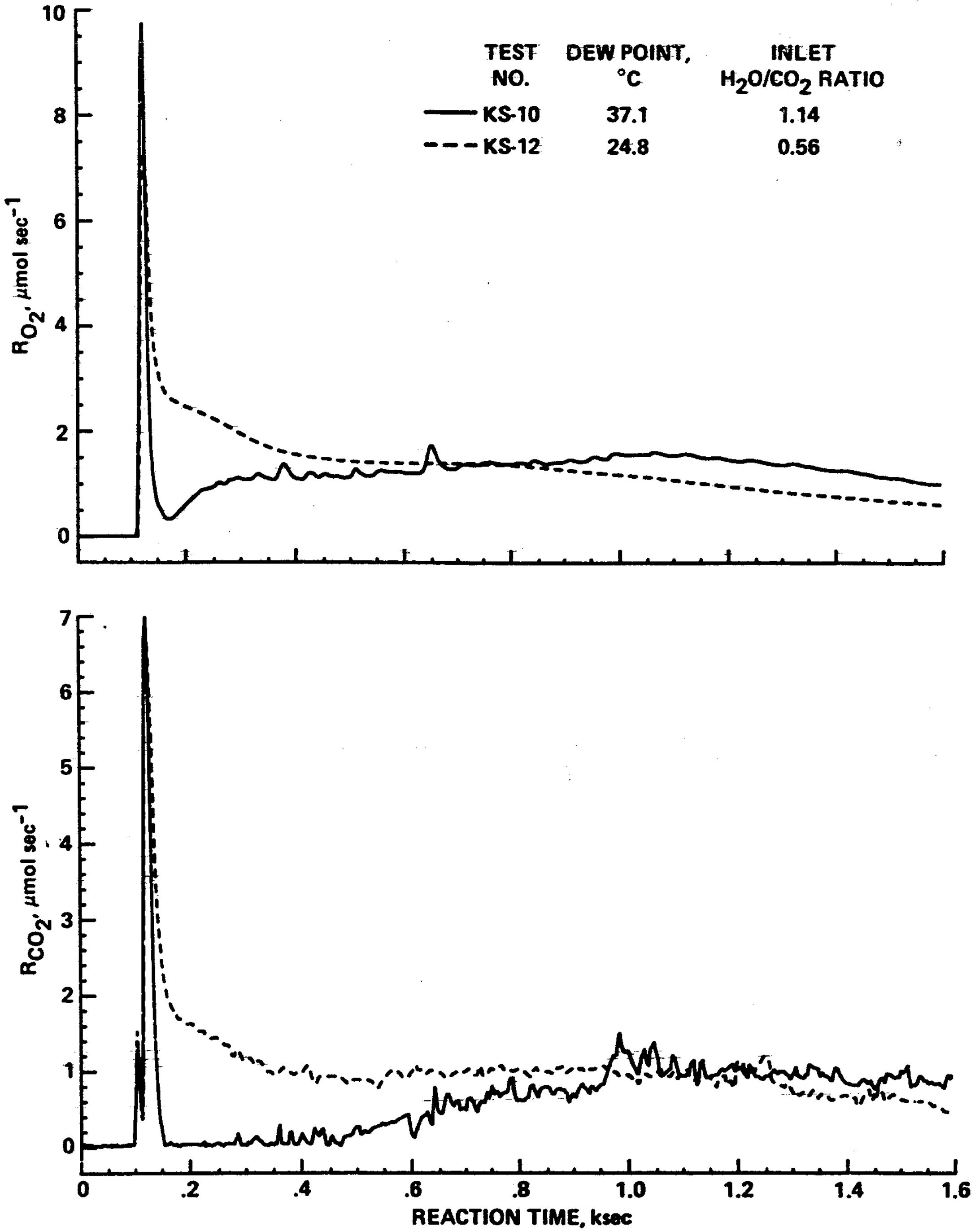


Figure 9.- Reaction of KO_2 tablets with humidified carbon dioxide/helium. Rates of O_2 evolution and CO_2 absorption as a function of reaction time at 1-atm total pressure.

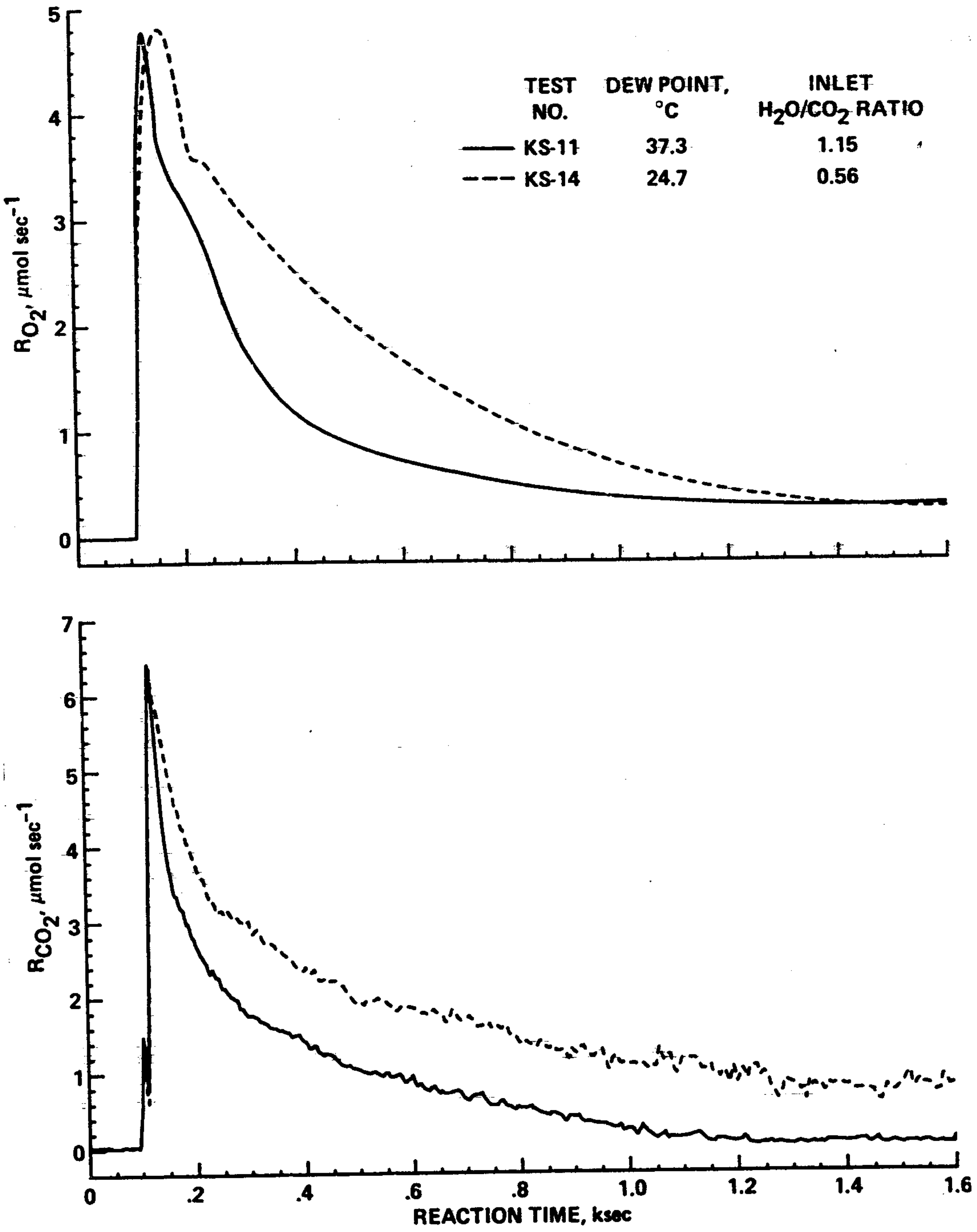


Figure 10.- Reaction of KO_2 granules with humidified carbon dioxide/helium. Rates of O_2 evolution and CO_2 absorption as a function of reaction time at 1-atm total pressure.

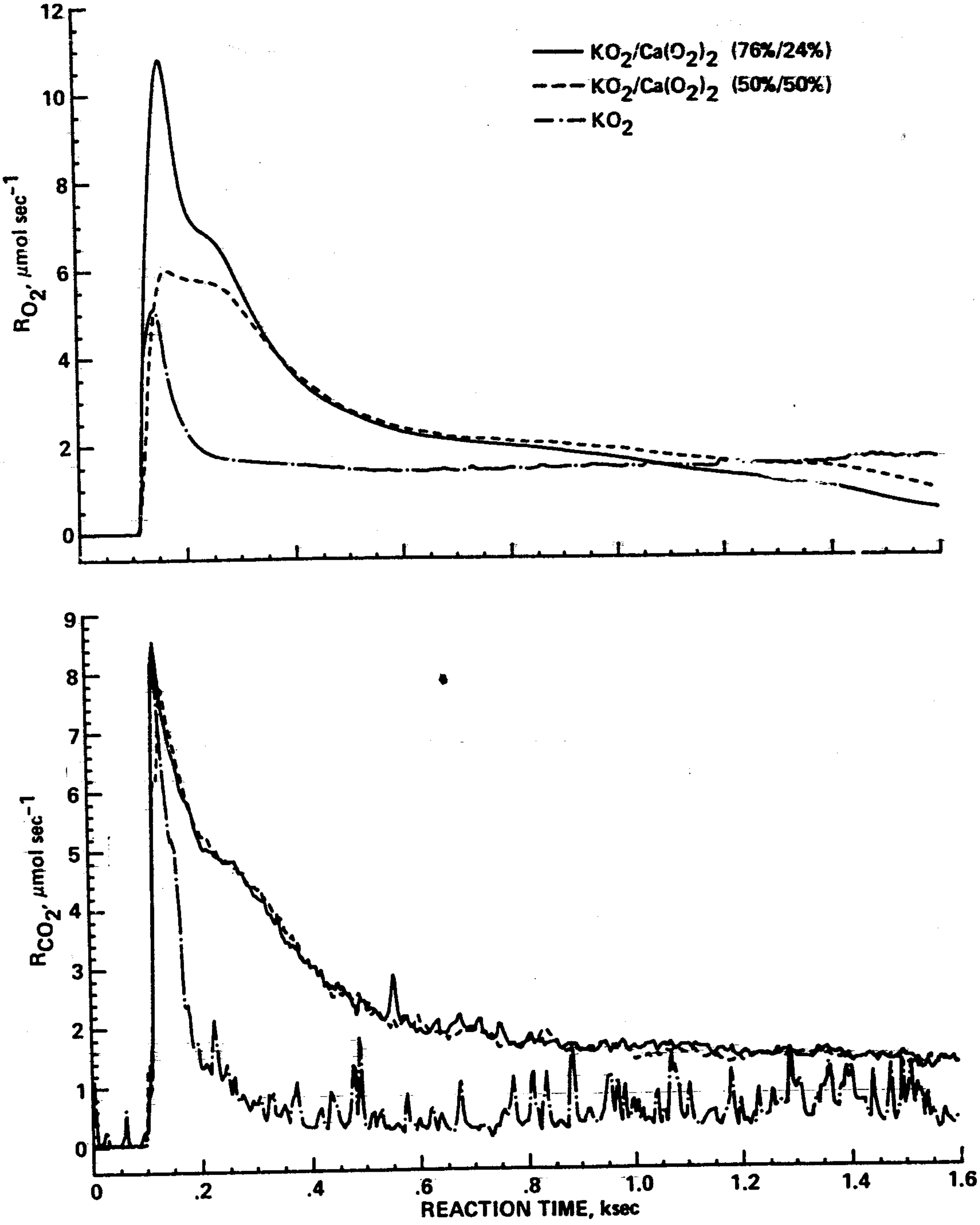


Figure 11.- Reaction of KO_2 and $KO_2/Ca(O_2)_2$ pellets with humidified carbon dioxide/helium. Rates of O_2 evolution and CO_2 absorption as a function of reaction time at 1-atm total pressure.

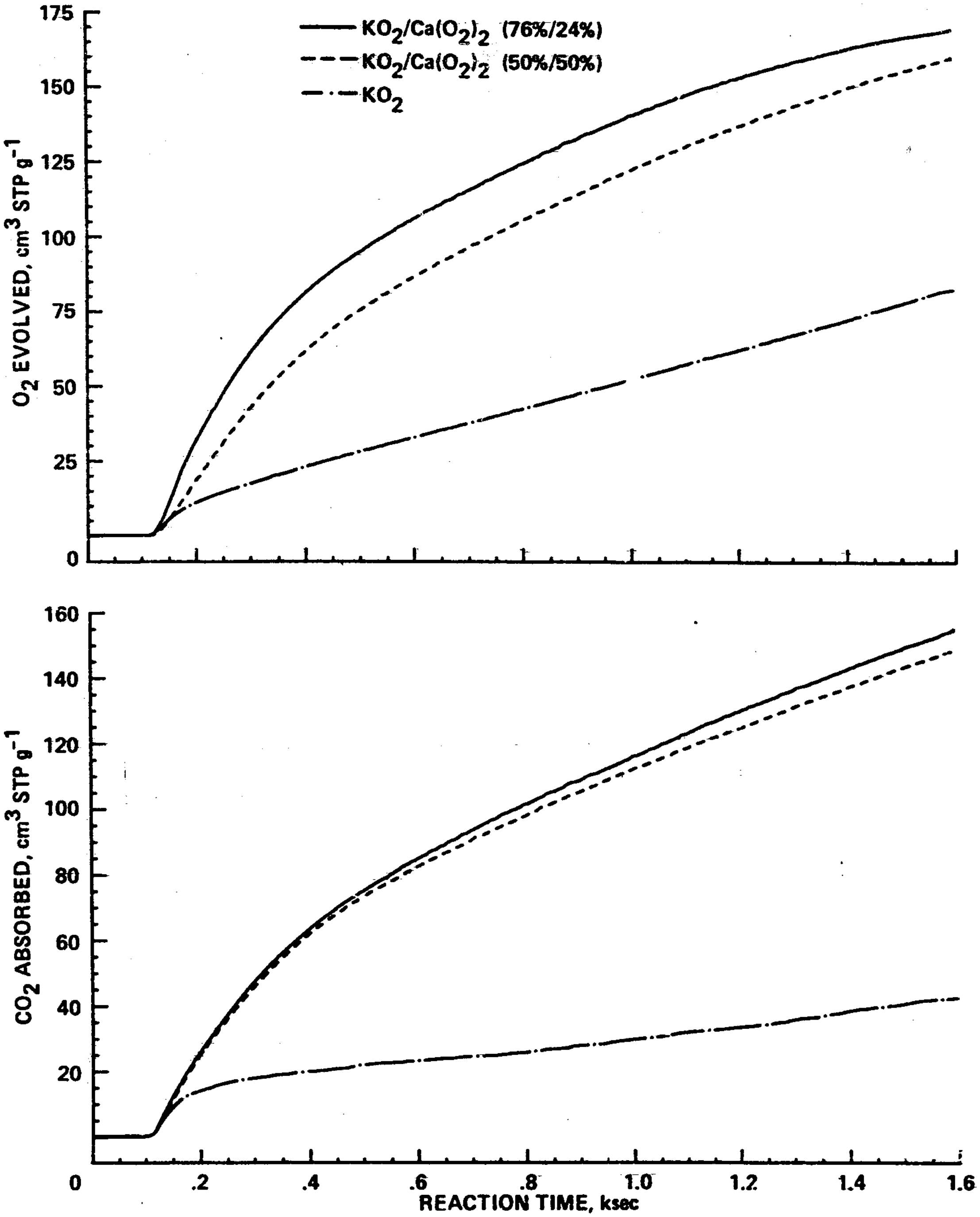


Figure 12.- Reaction of KO_2 and $KO_2/Ca(O_2)_2$ pellets with humidified carbon dioxide/helium. Amounts of O_2 evolved and CO_2 absorbed as a function of reaction time at 1-atm total pressure.

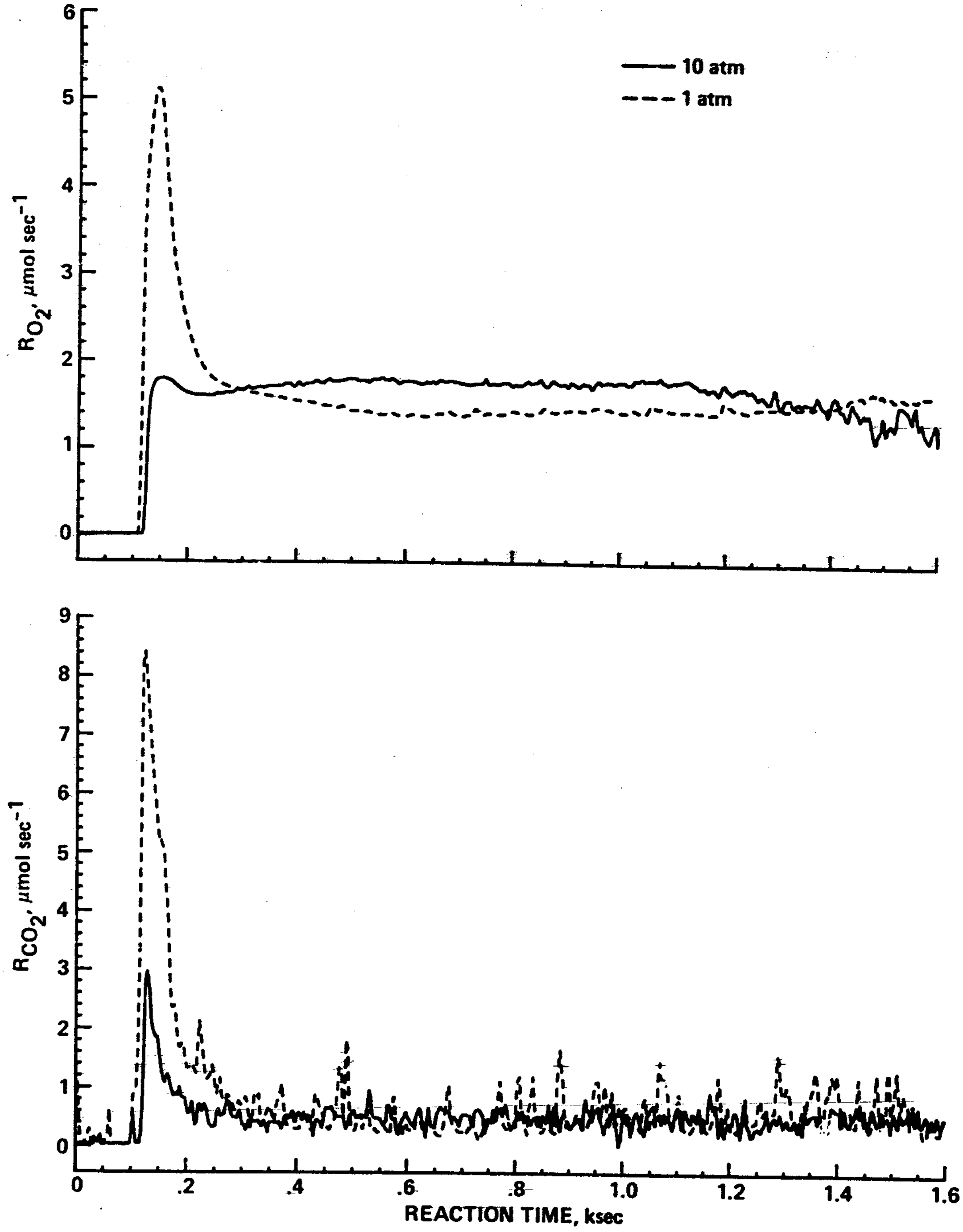


Figure 13.- Reaction of KO_2 pellets with humidified carbon dioxide/helium. Rates of O_2 evolution and CO_2 absorption as a function of reaction time at total pressures of 1 and 10 atm (test Nos. KS-2 and KS-3, respectively).

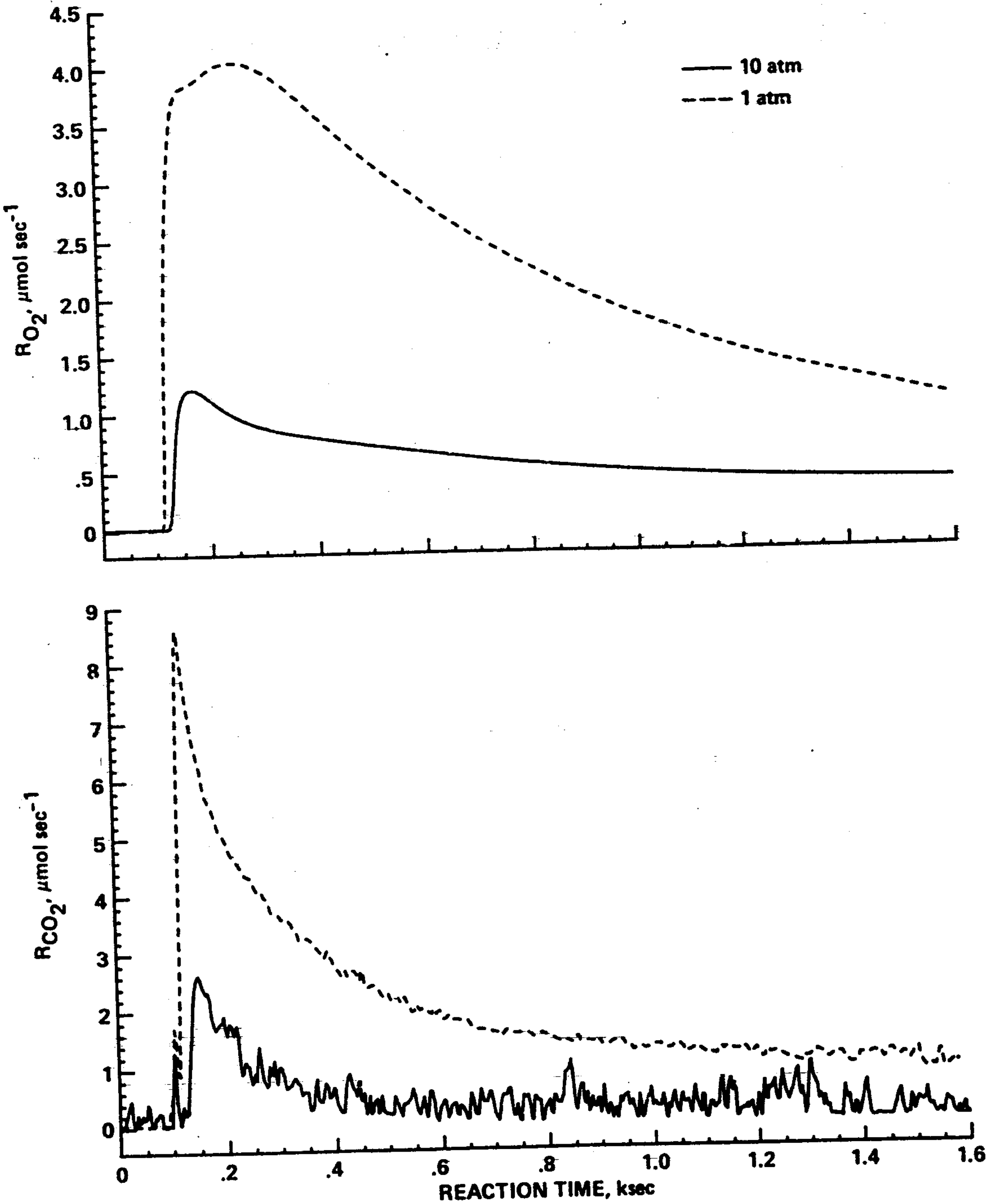


Figure 14.- Reaction of KO_2 pellets with humidified carbon dioxide/helium. Rates of O_2 evolution and CO_2 absorption as a function of reaction time at total pressures of 1 and 10 atm (test Nos. KS-6 and KS-7, respectively).

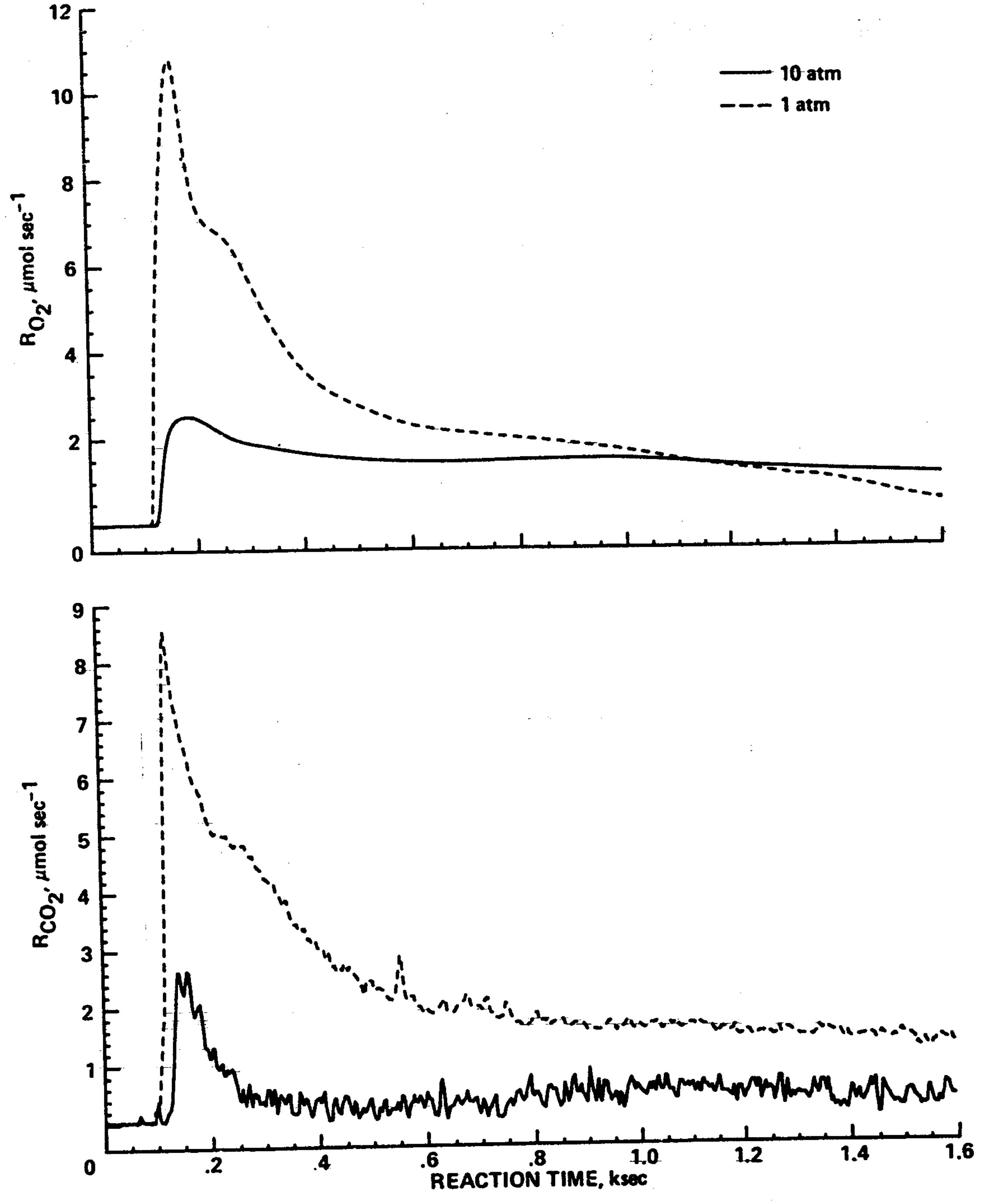


Figure 15.- Reaction of $KO_2/Ca(O_2)_2$ pellets with humidified carbon dioxide/helium. Rates of O_2 evolution and CO_2 absorption as a function of reaction time at total pressures of 1 and 10 atm (test Nos. KS/CaS-1 and KS/CaS-2, respectively).

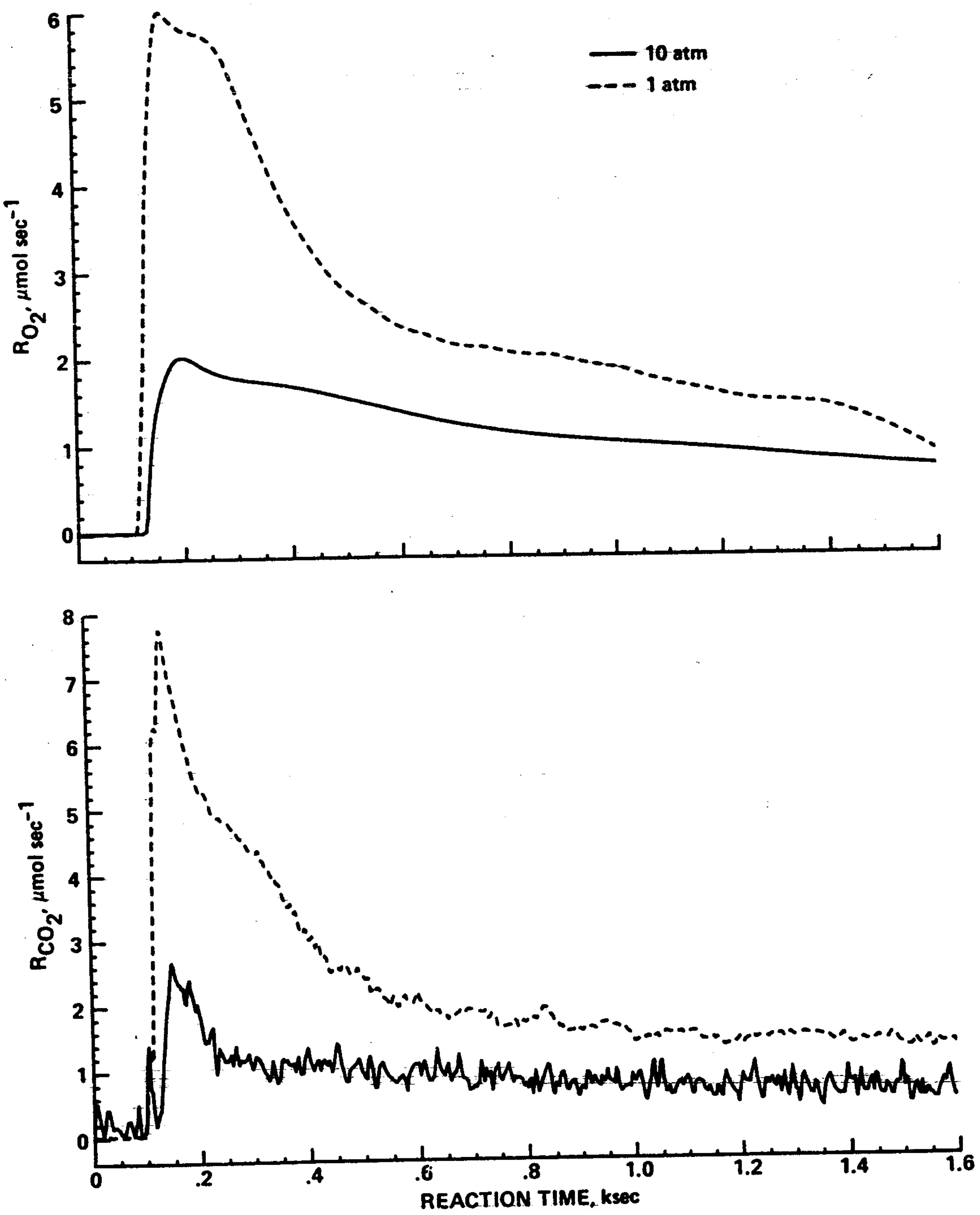


Figure 16.- Reaction of $KO_2/Ca(O_2)_2$ pellets with humidified carbon dioxide/helium. Rates of O_2 evolution and CO_2 absorption as a function of reaction time at total pressures of 1 and 10 atm (test Nos. KS/CaS-3 and KS/CaS-4, respectively).

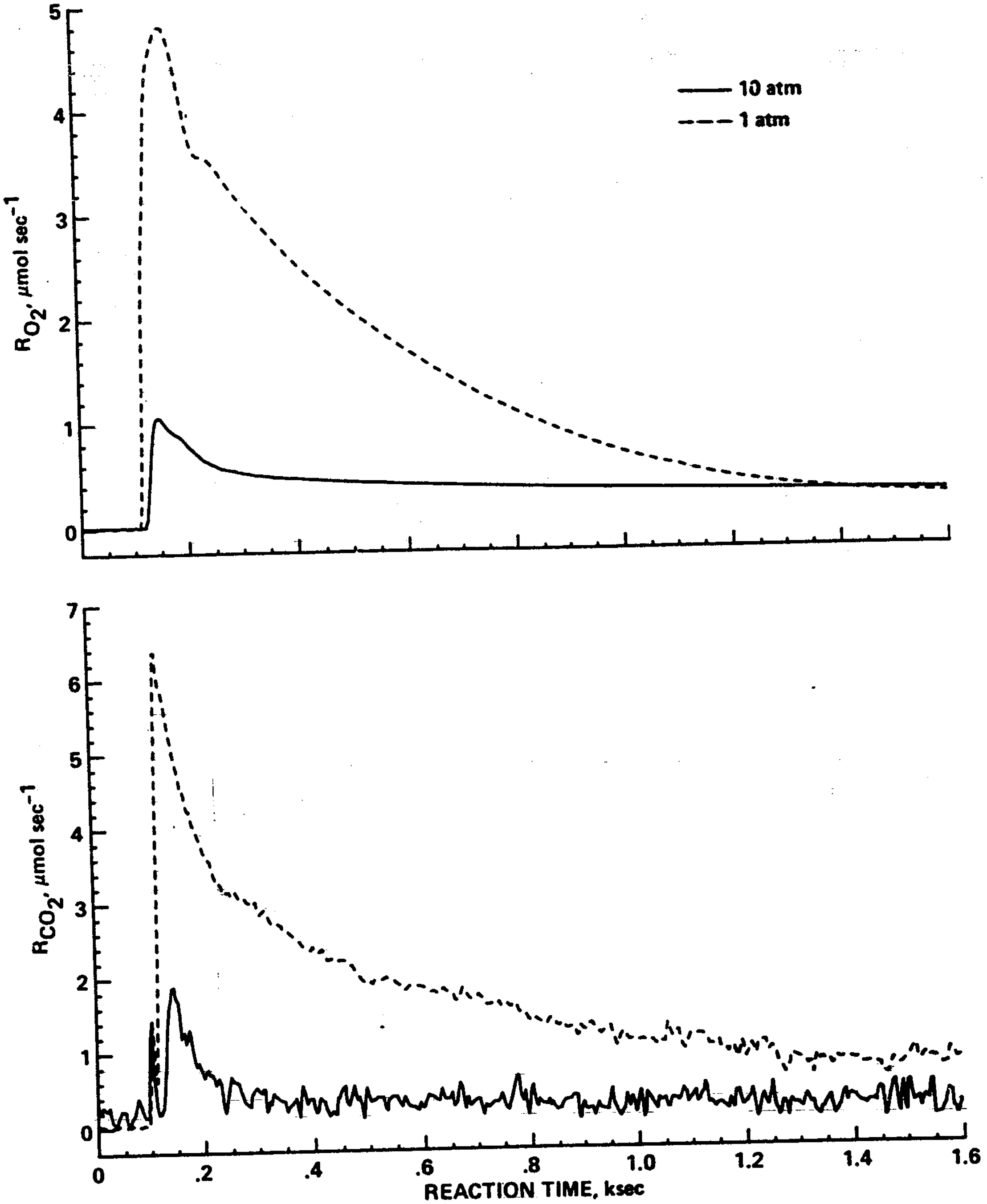


Figure 17.- Reaction of KO_2 granules with humidified carbon dioxide/helium. Rates of O_2 evolution and CO_2 absorption as a function of reaction time at total pressures of 1 and 10 atm (test Nos. KS-14 and KS-16, respectively).

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16. Abstract

In portable breathing apparatus applications at 1 atm, potassium superoxide (KO_2) has exhibited low-utilization efficiency of the available oxygen (O_2) and diminished carbon dioxide- (CO_2) scrubbing capacity caused by the formation of a fused, hydrated-hydroxide/carbonate product coating on the superoxide granules. In earlier work, it was discovered that granules fabricated from an intimate mixture of KO_2 and calcium superoxide, $Ca(O_2)_2$, did not exhibit formation of a fused product coating and the utilization efficiency with respect to both O_2 release and CO_2 absorption was superior to KO_2 granules when both types of granules were reacted with humidified CO_2 under identical conditions. In the work described here, single pellets of KO_2, $KO_2/Ca(O_2)_2$ mixtures and commercially available KO_2 tablets and granules were reacted with a flow of humidified CO_2 in helium at 1- and 10-atm total pressure and at an initial temperature of 40°C. In the 1-atm flow tests, the reaction rates and utilization efficiency of the $KO_2/Ca(O_2)_2$ pellets were markedly superior to the KO_2 pellets, tablets, and granules when the samples were reacted under identical conditions. However, at 10 atm, the rates of O_2 release and CO_2 absorption, as well as the utilization efficiencies of all the superoxide samples, were one-third to one-eighth of the values observed at 1 atm. The decrease in reaction performance at 10 atm compared to that at 1 atm has been attributed principally to the lower bulk diffusivity of the CO_2 and H_2O reactants in helium at the higher pressure and secondarily to the moderation of the reaction temperature caused by the higher heat capacity of the 10-atm helium.

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